M. Tech (Research) Thesis

On

Phase Transfer Catalyzed Reaction for Synthesis of Sulfides and Disulfides using Hydrogen Sulfide

Submitted by

Priya G. Nakade

612CH101

Under the Joint Supervision of

Prof. Sujit Sen

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DEPARTMENT OF CHEMICAL ENGINEERING

NATIONAL INSTITUTE OF TECHNOLOGYROURKELA

CERTIFICATE

This is to certified that the thesis entitled **"Phase Transfer Catalyzed Reaction for Synthesis of Sulfides and Disulfides using Hydrogen Sulfide"** submitted by **Priya Ganesh Nakade** to National Institute of Technology Rourkela, India for the award of degree of **Master of Technology (Research)** in engineering, is a bonafide record of investigation carried out by her in Department of Chemical Engineering, under the guidance of **Prof. Sujit Sen** and **Prof. Raghubansh Kumar Singh**. The report is up to the standard of fulfilment of M. Tech (Res.) degree as prescribed by regulation of this institute.

Prof. Sujit Sen

Prof. Raghubansh Kumar Singh

Date:

Dept. of Chemical Engineering

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PRIYA GANESH NAKADE

(612CH101)

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LIST OF SYMBOLS

Q^+X^-	Phase Transfer Catalyst
Q^+	Quaternary Ammonium Cation
MY	Aqueous Phase Reactant
RX	Organic Product
RY	Desired Product
K^{nc}	Reaction Rate Constant of Non Catalytic Reaction
K^c	Reaction Rate Constant of Catalytic Reaction
Q_0	Total Initial Catalyst Added
K	Dissociation Equilibrium Constants
m	Distribution Coefficient
T_s	Total Sulfide Concentration
T_{MDEA}	Total MDEA Concentration

LIST OF ABBREVIATIONS

BC	Benzyl Chloride
BM	Benzyl Mercaptan
DBS	Dibenzyl Sulfide
GLC	Gas liquid chromatography
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
PTC	Phase Transfer Catalysis
TBPB	Tetrabutylphosphonium Bromide

ABSTRACT

This study focuses on utilization of hydrogen sulfide (H_2S) in the synthesis of fine chemicals such as Dibenzyl Sulfide (DBS), Benzyl Mercaptant (BM) and Dibenzyl Disulfide (DBDS). This involves first absorption of H_2S in either aqueous ethanolamine (MEA) or methyldiethanolamine (MDEA) and then reaction of this H_2S richaqueous solution with organic reactants. Two reaction systems have been studied in the present work – first being the reaction of benzylchloride (BC) with H_2S rich aqueous MDEA in the presence of Tetrabutyl Phosphonium bromide (TBPB) as a PT catalyst under liquid-liquid (L-L) phase transfer catalysis to synthesize DBS and BM and in second system, DBDS was synthesized by adding sulfur powder in H_2S rich aqueous MEA using Amberlite IR-400 as a PT catalyst at liquid-liquid-solid (L-L-S) PTC. The overall objective of this study is to maximize conversion of reactant, maximize selectivity of desired product, searching for mechanism and calculation of kinetic parameter. In all the systems under study, desirable products were obtained with 100% selectivity at some level of process parameters. Reaction time, temperature,catalyst loading, stirring speed, reactants concentration and solvent concentration were chosen as reaction parameters. Amberlite catalyst was recovered and reused 4 times with successive decrease in BC conversion in each run.

Keywords: Absorption of H_2S in amines, Phase Transfer Catalysis, Benzyl Mercaptant, Dibenzyl Sulfide, Dibenzyl Disulfide, Tetrabutyl Phosphonium Bromide, Amberlite IR-400.

CONTENTS

Chapter 1
INTRODUCTION

Many valuable reactions cannot be carried out due to insoluble nature of reactants in one solvent. Conventionally a solvent is selected which can dissolve all the reactants in to it but use of such solvents are not always economical since these solvents are highly expensive in nature. Also, the rate of reaction obtained is too low due to excessive solvation of the nucleophile and has a difficulty of separation of valuable product from reaction mixture. To solve this problem, reactants are allowed to dissolve in their respective aqueous and organic solvents and then catalyst is added to transfer the reactant from the aqueous or solid phase into the organic phase, where reaction occurs. The phenomenon is called as phase transfer catalysis (PTC) and catalyst used is called as phase transfer (PT) catalyst.

Thus, reaction is made possible by bringing together the reagents which are originally in different phases. Now a day, PTC is a matured technology used in more than 600 synthesis application covering pharmaceuticals, perfumes, agrochemicals, flavors, dyes, polymer industries, pollution control technologies etc. PTC has proved a better than traditional synthesis method because of its mild operating condition, use of cheaper reagents, high selectivity of product in shorter time and suppression of unwanted side reactions. (Weber and Gokel, 1977; Selvi et al., 2012).

1.1 MECHANISM

The mechanism of PTC reaction was first proposed by Stark's in 1971. Fig. 1.1 shows the overview of PT mechanism.

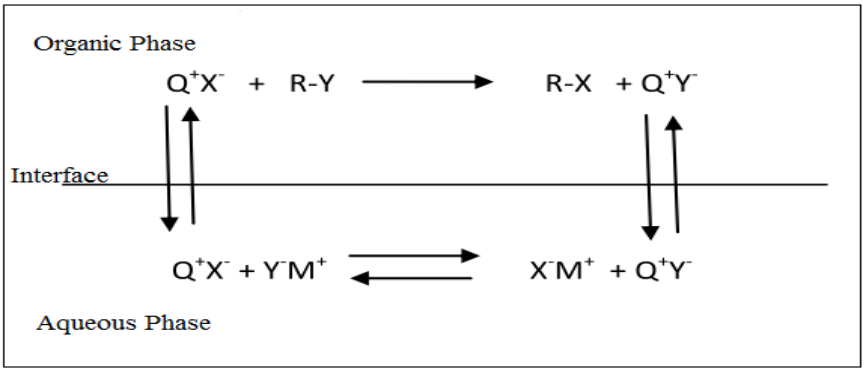


Figure 1.1: Stark's Mechanism of PTC

According to Stark's Mechanism, first ion exchange reaction takes place in between anion of the reactant (Y^-M^+) and PT catalyst (Q^+X^-) dissolved in the aqueous phase. The formed ion-pairs (Q^+Y^-), due to its lipophilic nature, travel from aqueous phase to organic phase by crossing liquid-liquid interface. This step is called as a phase transfer step. In second step, the transferred ion pair undergoes a nucleophilic substitution reaction with organic reagent (RX) to give a desired product (RY) shown in Fig. 1.1. The PT catalyst (Q^+X^-) then subsequently returns from organic phase to the aqueous phase and cycle continues (Starks, 1985; Hashimoto and Maruoka, 2008).

1.2 PHASE TRANSFER CATALYST

The primary requirements of PT catalyst are

- Catalyst should be sufficiently lipophilic in nature to transfer nucleophilic anion from aqueous phase to organic phase.
- It should have good partition coefficient between aqueous and organic phase.
- Catalyst should form loose cation-anion bonding so that cation should be easily available for anion exchange reaction in aqueous phase.

The commonly used agents for phase transfer catalyst are onium salts (ammonium and phosphonium salts), crown ethers, cryptands and open chain polyethers like polyethylene glycols (PEG) shown in Fig. 1.2 below (Nathan, 2011).

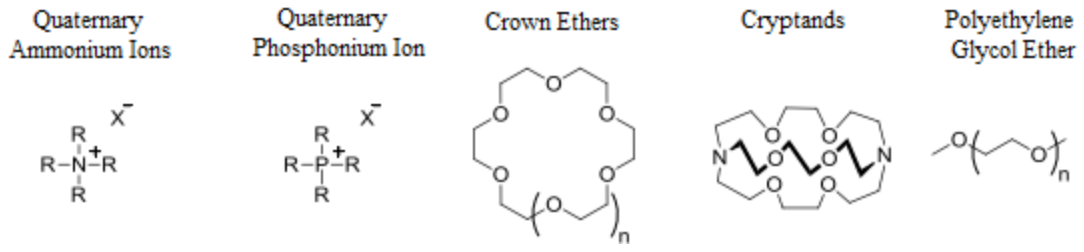


Figure 1.2: Commonly used effective PT Catalyst

Catalyst is selected on the basis of its nature under reaction condition, toxicity, activity, ease of preparation or availability and ease of recovery or recycle. Table 1.1 shows the properties of commonly used PT catalyst.

Quaternary onium salts undergo degradation at high temperature and in a presence of strong base. At a high temperature (100-200^{0}C), onium salts have tendency to undergo internal displacement reaction shown in reaction 1.1 to give trialkylamine and displacement reaction.

$$R_4N^+Y^- \rightarrow R_3N + RY \quad (1.1)$$

And in the alkaline condition, it decomposes by Hoffmann elimination reaction shown in reaction 1.2 to yield trialkylamine and olefin (Jing, 2003).

$$R'CH_2CH_2NR_3 + OH^- \rightarrow R'CH = CH_2 + R_3N + H_2O \quad (1.2)$$

Table 1.1: Properties of Commonly Used PT Catalyst (Naik and Doraiswamy, 1998)

Catalyst	Cost	Stability and activity	Use and recovery of catalyst
Ammonium Salt	Cheap	Moderately active. Decomposes by reaction 1.1 and reaction 1.2 shown above.	Commonly used but difficult to recover.
Phosphonium salt	Costlier than ammonium salts	Moderately active. Thermally more stable than ammonium salt but decomposes under basic condition.	Commonly used but difficult to recover.
Crown ethers	Expensive	Highly active. Stable at both high temperature and basic condition.	Often used. Difficult to recover due to toxicity.
Cryptands	Expensive	Highly active. Stable at both high temperature and basic condition.	Used sometimes due to high activity. Recovery is difficult due to toxicity.
PEG	Very cheap	Lower activity but more stable than onium salts.	Rarely used where high concentration of catalyst does not affect the synthesis reaction. Easy to recover.

So in short, on the basis of activity, cost, toxicity, availability, (Q^+X^-) quaternary onium salts are the most economical and feasible PT catalyst and are used in various synthesis processes. PEG has less industrial applications due to its lower activity. Crown ethers and cryptands are useful in the reaction condition where onium salt and PEG are not useful but its cost and toxicity generally restricts its application.

Among the various quaternary onium salt, a lipophilic cation (Q^+) is selected for the effective anion transfer and good compatibility with organic phase. Onium salts like tetrabutyl onium halide have good partition coefficient between aqueous and organic phase and hence mostly preferred for industrial use. The highly hydrophilic catalyst like tetramethyl ammonium salt is not chosen because of its high solubility with aqueous phase than organic phase. But continuous increase in alkyl chain to increase the lipophilicity is also not desirable since it makes the catalyst highly lipophilic and decreases its partition coefficient (Halpern, 2009; Jing, 2003).

1.3 CLASSIFICATION OF PTC

Soluble and Insoluble PTC are two main classes of PTC reactions shown in Fig. 1.3. Soluble PTC is further classified in to liquid-liquid (L-LPTC), gas-liquid (G-LPTC) and solid-liquid PTC (S-LPTC) according to actual aqueous and organic phases present. But separation of product and recovery of catalyst is difficult in soluble PTC. Hence, in order to increase the recovery and reuse of PT catalyst, a catalyst rich layer is created in between aqueous and organic phase, and this type is known as insoluble PTC.

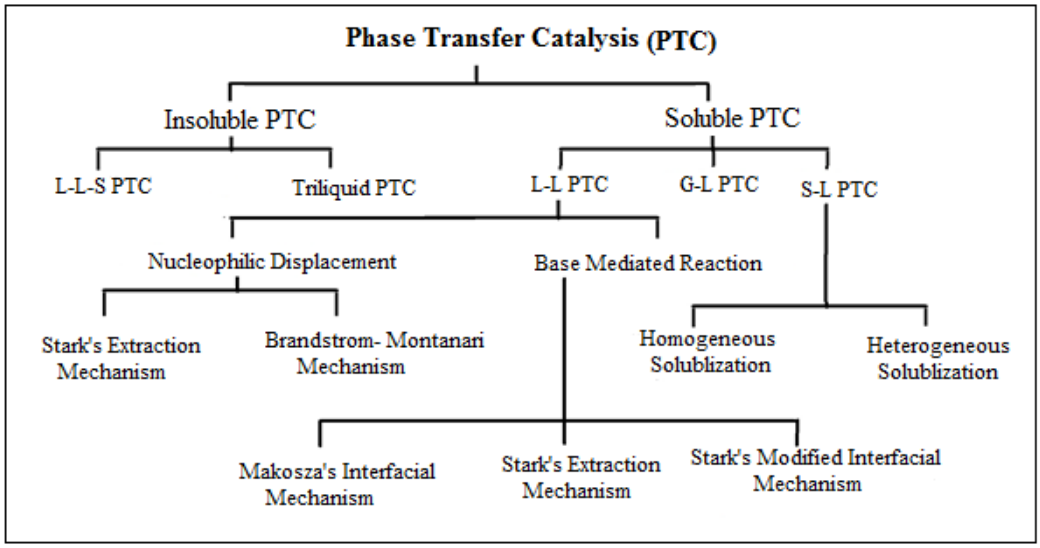


Figure 1.3: Classification of PTC

1.3.1 Soluble PTC

1.3.1.1 Liquid-Liquid (L-L) PTC

In L-L PTC, nucleophile M^+Y^- dissolves in aqueous phase while organic reaction with organic reactant RX takes place in organic phase. Stark's Extraction Mechanism is discussed in

Fig. 1.1 above. In Stark's Extraction Mechanism, the catalyst used is both lipophilic and hydrophilic in nature, so that it should be distributed in both aqueous and organic phase. But in Brandstrom Montanari Mechanism, catalyst is too lipophilic in nature that it resides only in organic phase. So ion exchange reaction between quant (Q^+X^-) and aqueous reactant (M^+Y^-) occurs at or near the interface of aqueous and organic phase shown in Fig. 1.4 (Starks et al., 1994; Wu, 1993; Fiamegos et al., 2006).

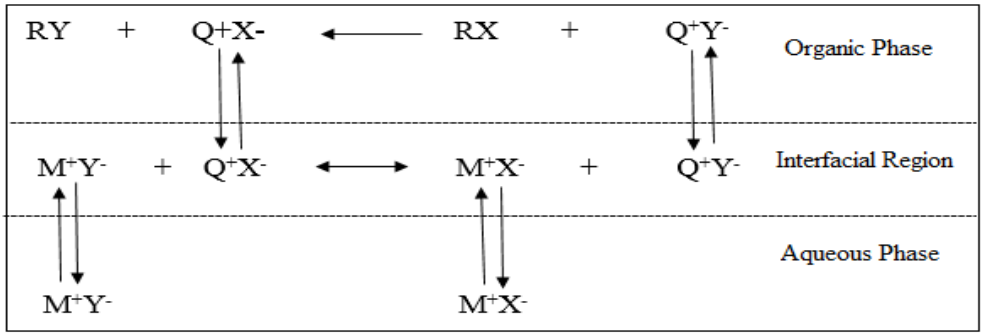


Figure 1.4: Brandstrom Montanari Mechanism

1.3.1.2 Solid-Liquid (S-L) PTC

Usually more industrial applications are found with L-LPTC but suffer from the problem of unwanted side reaction of hydrolysis. To eliminate this, nucleophile is taken in solid form suspended in organic phase, called as solid-liquid (S-L) PTC. Thus, more yield and selectivity can be achieved through S-LPTC than L-LPTC.

During the reaction, quant (Q^+X^-) first move to solid nucleophile for the ion exchange reaction at or near the solid surface to form active form of catalyst Q^+Y^-. On the basis of location of this ion exchange reaction, S-LPTC is further classified to homogeneous and heterogeneous solubilization. In homogeneous solubilization, nucleophiles (KY) have some limited solubility in organic phase and get dissolve in solid liquid interface. So quant does not directly come in contact with solid surface and ion exchange reaction takes place with dissolved KY at interface. Whereas, in heterogeneous solubilization, quant has to go to surface of solid crystal lattice for ion exchange and ferries back to organic phase shown in Fig. 1.5. The synthesis reaction of QY with organic substrate RX takes place in bulk of organic phase (Melville and Goddard, 1988).

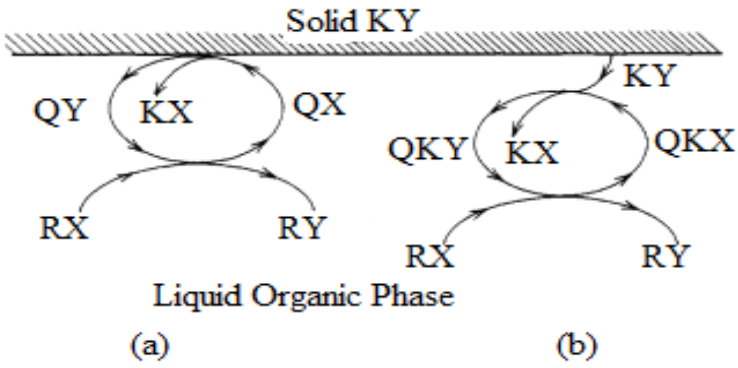


Figure 1.5: (a) Heterogeneous (b) Homogeneous S-LPTC

1.3.1.3 Gas-Liquid PTC

The PTC in gas-liquid-solid mode is called as gas-liquid G-LPTC. Here, the gaseous phase, contained organic substrate, is passed over a bed of solid inorganic reagent coated with PT catalyst in molten liquid form shown in Fig. 1.6 below. The gaseous reactant RX diffuses through molten PT catalyst for organic synthesis. Though, it is a tri-phase system, traditionally referred as a GLPTC.

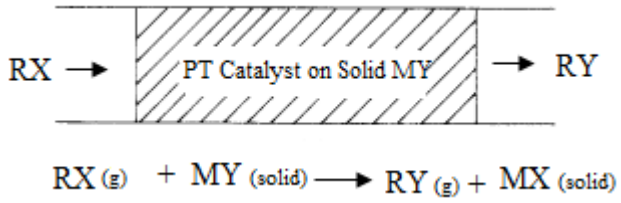


Figure 1.6: Mechanism of G-L PTC

The advantages of G-LPTC over L-LPTC are its continuous mode of operation through constant flow of organic gaseous reactant over solid bed. PT catalyst can easily recovered as it is directly loaded on inorganic solid bed and increased selectivity is obtained due to absence of unwanted side reaction of hydrolysis.

But in order to obtain an organic reactant in gaseous form, process is carried out at a high temperature. High temperature may be sometimes responsible for thermal decomposition and fractional volatilization of PT catalyst. So the selected catalyst should have sufficient thermal stability (Tundo et al., 1989).

1.3.2 Insoluble PTC

In above systems, separation of catalyst and product from reaction mixture is done by using some unit operation processes like distillation, extraction and absorption. But distillation becomes an energy consuming process if the relative volatility between product, catalyst and solvent are too low. Additional solvent is required in case of extraction and absorption which again has to be distilled off (Yadav and Lande, 2005; Yadav and Desai; 2005). Therefore, catalyst is generally a waste due to its small quantity than product (Jin et al., 2003).

These problems can be solved by converting biphasic PTC to tri-phasic system namely liquid-liquid-solid (L-L-S) PTC and liquid-liquid-Liquid (L-L-L) PTC (Yadav and Motirale, 2010).

1.3.2.1 Liquid-Liquid-Solid PTC

L-L-S PTC contains dispersed organic phase containing substrate, continuous aqueous phase containing reagent and a solid supported PT catalyst. Like a stark's extraction mechanism, its mechanism also involves ion exchange step in aqueous phase and synthesis reaction step in organic phase. But in L-LPTC, catalyst is free to move between aqueous and organic phase while in L-L-S PTC, moment of catalyst is restricted and aqueous and organic phase travels inside the catalyst to react with catalyst cation (Satrio et al., 2000). Fig. 1.7 shows systematic representation of L-L-S PTC mechanism.

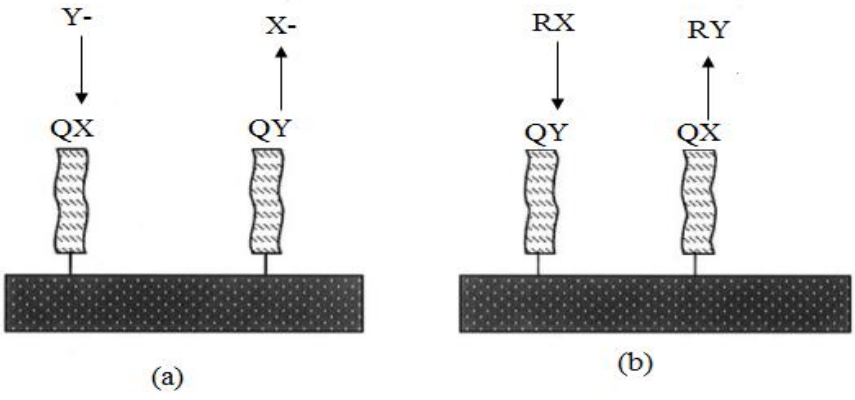


Figure 1.7: (a) Aqueous Phase Reaction (b) Organic Phase Reaction Mechanism of L-L-S PTC

1.3.2.2 Liquid-Liquid-Liquid PTC

In L-L-S PTC, catalyst is bounded on solid matrix like polymer or inorganic support. The catalyst can be easily separated from reaction mixture by filtration and reused. But rate of reaction is limited due to intra-particle diffusion limitations and also has high initial cost of catalyst preparation. To overcome from all these problems, a conventional L-L system is converted to tri-liquid L-L-L PTC in which a middle catalyst rich phase is created in between aqueous and organic phase where a reaction occurs through a proper balance of density, hydrophilicity, interfacial tension, lipophilicity and phase equilibrium.

Third liquid phase can be created either by increasing catalyst concentration above critical value or through saturation of aqueous phase. Existence of catalyst rich phase is recorded with sudden increase in reaction rate with 100% selectivity of desired product in relatively less reaction time. The catalyst rich phase can be easily separated and reused since it is immiscible in aqueous and organic phase. In L-L-L PTC, organic phase never come in contact with aqueous phase so unwanted side reactions of hydrolysis are avoided giving high selectivity of product.

The main advantages of L-L-L PTC are i) high conversion with mild reaction conditions ii) easy recovery of catalyst and its reuse iii) high yield of desired product due to suppression of unwanted side reactions iv) no need of solid support for catalyst. L-L-L PTC also suffers from disadvantage of high quantity of catalyst requirement giving high initial cost of operation. But catalyst can be easily recovered and reused. Catalyst recovery can be done either reuse of only catalyst rich phase or reuse of catalyst rich phase along with aqueous phase. There is always decrease in catalyst activity through each run due to loss catalyst in aqueous and organic phase distribution (Yadav and Badure, 2007). The L-L-L PTC mechanism is shown in Fig. 1.8 below.

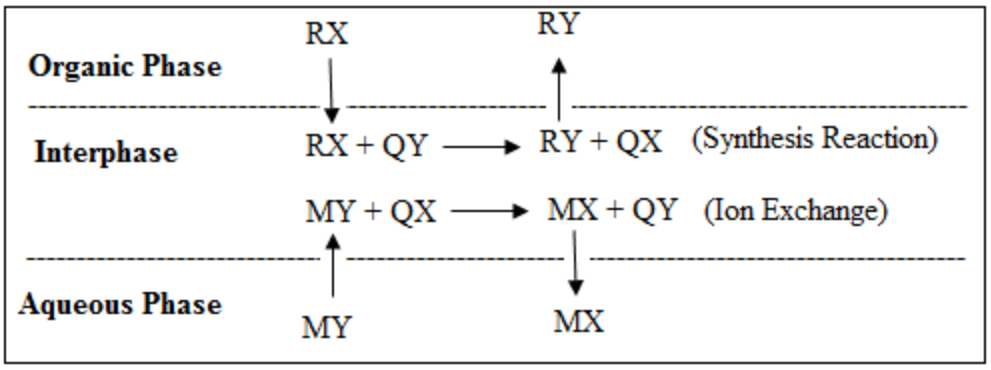


Figure 1.8: Mechanism of L-L-L PTC

1.4 PRESENT WORK

The present work deals with finding out substitute method of H_2S removal and sulfur recovery processes for enhancing utilization of H_2S present in different gas streams. The work is undertaken for the synthesis of various valuable chemicals like Dibenzyl Disulfide (DBDS) and Dibenzyl Sulfide (DBS) from H_2S rich gas streams obtained from various industries which is generally treated as a waste by absorbing it in various amines like Ethanolamine (MEA) and Methyldiethanaol amine (MDEA). The present work involves

- Synthesis of DBS from Benzyl Chloride (BC) and H_2S rich MDEA using Tetrabutylphosphonium bromide (TBPB) as a PT catalyst under L-LPTC condition.
- Synthesis of DBDS from BC and H_2S rich MEA by adding adequate quantity of sulfur powder in aqueous phase under triphase L-L-SPTC in presence of Amberlite IR-400 as a PT catalyst.
- Study of effect of different process parameters like stirring speed, concentrations of reactant and catalyst, sulfide and amine concentrations in aqueous phase, temperature and sulfur powder loading for increasing conversion and selectivity of desired product.
- Establishment of reaction mechanism to find out pathway of synthesis process.
- Estimation of reaction parameters like order of reaction, activation energy etc.

1.5 SOURCES AND NEED OF H_2S REMOVAL

H_2S gas having smell of rotten eggs is a colorless, poisonous and flammable gas generated both from naturally and manmade processes. Natural sources of H_2S include sulfur springs,

volcanoes, crude petroleum and natural gas. Manmade sources originates from various industries like petroleum refineries, natural gas processing plants, coke oven plants, petrochemical plants etc. (Toxological Profile of hydrogen sulfide, 2006).

H_2S gas present in atmosphere changes itself to sulfur dioxide and sulfuric acid by staying in atmosphere for an average of 18 hrs. It is also responsible for corrosion and cracking of metals to break tanks and piping system by combining with water. Therefore, removal of H_2S from the process stream is very essential for protecting process devices and safety of human health. Even a small concentration of H_2S can affect the human body through irritation in nose, eyes and throat and the high concentration (> 500 ppm) can cause permanent loss of consciousness or sometimes even death (Huertas et al., 2001; Syed et al.; 2006).

1.6 INDUSTRIAL PROCESSES FOR REMOVAL AND RECOVERY OF H_2S

Various processes like absorption, adsorption, membrane technology and biological removal are used for removal of H_2S from gas steam.

In adsorption process, numerous adsorbents like carbon, metal based adsorbents like (Fe, Ti, Cr, Zn, Al) are used but can be reused only 2-3 times. Membrane separation process is easy to install and use but its efficiency is too low. Biological separation is also not an economical process due to its maintenance and difficulty in controlling process.

Therefore, absorption of this weak inorganic acid in base is considered as a best process for recovery and removal of H_2S from gas stream. Absorption bases include alkaline solutions, aqueous ammonia, alkanolamine and sodium and potassium carbonate solutions. Good efficiency is obtained with strong base NaOH but selective absorption is not possible with other associated gases like CO_2. To overcome from this problem, weak alkali solutions like ammonia (NH_3) and alkanolamines are used as an absorbent for removal and recovery of H_2S (Vago et al., 2011; Huertas et al., 2001).

1.6.1 Ammonia Based Processes

NH_3 is a commonly used absorbent for gases like carbonyl sulfide (COS), carbon disulfide (CS_2), hydrogen cyanide (HCN), pyridine bases, thiophenes, mercaptans, ammonia and traces of

nitric oxide at a room temperature. It is also used for absorbing CO_2 and H_2S impurities from the gas streams as shown in reaction Scheme 1.1.

$$NH_{3(aq)} + H_2S \leftrightarrow [NH_4]^+_{(aq)} + [HS]^-_{(aq)}$$

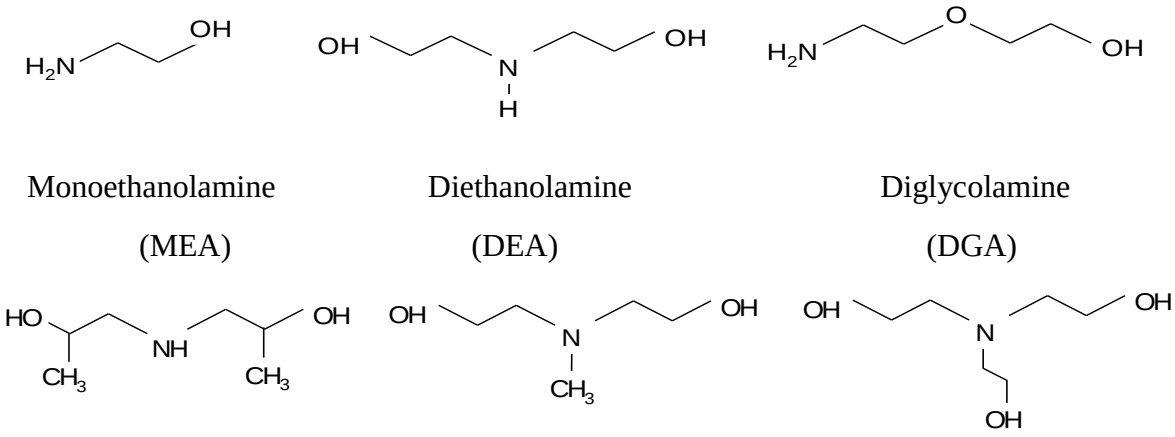
$$2NH_{3(aq)} + H_2S \leftrightarrow 2[NH_4]^+_{(aq)} + S^{2-}_{(aq)}$$

Scheme 1.1

But due to high partial pressure of process and difficulty in absorbent regeneration, it is not an industrially established process for H_2S recovery (Kohl and Nielsen, 1997).

1.6.2 Absorption in Alkanolamine

The commonly used alkanolamines for H_2S removal are shown in Fig. 1.9.



Monoethanolamine (MEA) | Diethanolamine (DEA) | Diglycolamine (DGA)

Diisopropanolamine (DIPA) | Methyldiethanolamine (MDEA) | Triethanolamine (TEA)

Figure 1.9: Commonly used Alkanolamine

Hydroxyl group attached to alkanolamine decreases vapor pressure and helps in increasing its water solubility and amine group makes aqueous solution basic in nature to dissolve acid gases like H_2S. The advantages and disadvantages of commonly used alkanolamine are shown in Table 1.2 below.

Table 1.2: Comparison of Various Alkanolamine (Warudkar et al., 2010)

Monoethanolamine (MEA)

Advantages

- Primary amine with very high reaction rate
- Easy recovery and low amine circulation rate
- Low molecular weight increases solution capacity at moderate concentration.

Drawbacks

- High heat of reaction
- MEA concentrations above 30 – 40 wt% and CO_2 loadings above 0.40 moles-CO_2/mole-amine are corrosive
- High volatility causes loss of amine in absorber overhead
- Selective absorption of H_2S is not possible.

Diethanolamine (DEA)

Advantages

- Low volatility and less reactive due to secondary amine
- Low heat of reaction
- Less corrosive than MEA
- Can be used for selective absorption of H_2S for gas stream containing sufficient amount of COS and CS_2 due to its low reactivity.

Drawbacks

- High amine circulation rate
- Selective absorption of H_2S is not possible with gas stream associated with CO_2 also.
- DEA concentration above 30 – 40 wt% CO_2 loading above 0.4 moles CO_2/mole-amine is highly corrosive.

Methyldiethanolamine (MDEA)

Advantages

- Selectively absorb H_2S from gas streams containing both H_2S and CO_2.
- Low desorption temperature and low heat of reaction compared to MEA and DEA.
- Less corrosive than MEA and DEA
- Can be used up to 60 wt% in aqueous solution due to its low vapor pressure.
- Because of low vapor pressure, MDEA can be used in concentration up to 60 wt% in aqueous solutions without appreciable amount of evaporation loses.

Drawbacks

- Costlier than MEA and DEA.

Scheme 1.2 represents basic chemical reactions involving in alkanolamine absorption process by considering a primary amine MEA (RNH_2) and its overall process is shown in Fig. 1.10.

Reactions with H_2S:

Sulfide formation: $2RNH_2 + H_2S \leftrightarrow [RNH_3]_2S$

Hydrosulfide formation: $RNH_2 + H_2S \leftrightarrow RNH_3SH$

Reactions with CO_2:

Carbonate formation: $2RNH_2 + CO_2 + H_2O \leftrightarrow [RNH_3]_2CO_3$

Bicarbonate formation: $RNH_2 + CO_2 + H_2O \leftrightarrow RNH_3CO_3H$

Carbamate formation: $2RNH_2 + CO_2 \leftrightarrow RNH - CO - ONH_3R$

Scheme 1.2

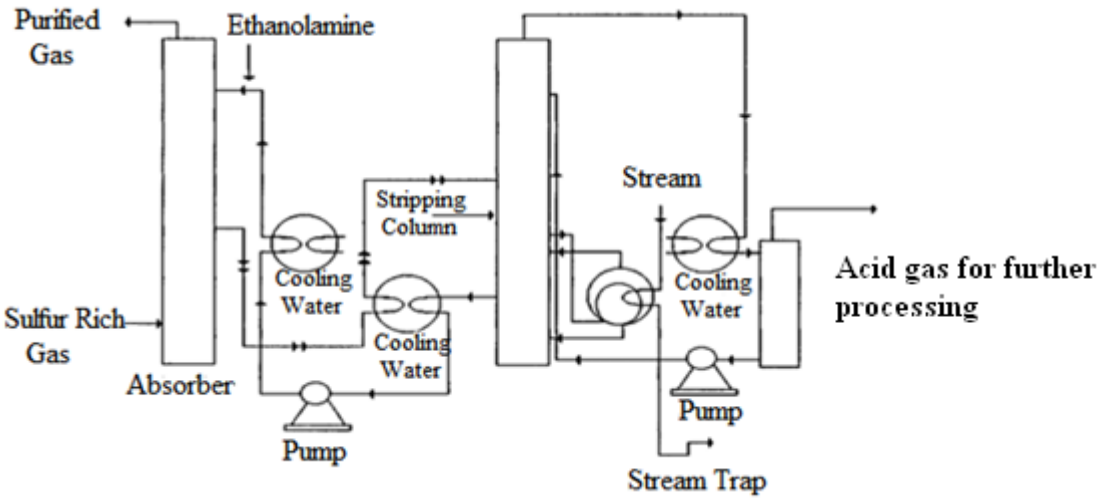


Figure 1.10: Schematic Diagram for Alkanolamine Acid Gas Removal Processes

Sulfur rich gas is injected at the bottom while MEA is circulated counter currently from the top of absorber. H_2S present in feedstock is absorbed by MEA and cleaned feedstock containing minute traces of sulfur is removed from the top. The H_2S rich MEA collected from bottom of an absorber is sent to the stripping column via heat exchanger. In stripping column, regeneration of absorbent takes place by passing absorbed H_2S again to the gas phase. The acid gas removed from the top of stripper is cooled down to isolate H_2S from water vapor for its further processing like sulfur recovery process via clause process. The hot regenerated MEA from the stripping column is used to heat H_2S-rich MEA escaping from absorber. The clean MEA is again cooled down and reused in absorption column. This process is also suitable for absorption of CO_2 (Zare and Mirzaei, 2009).

CHAPTER 2

LITERATURE SURVEY

2.1 BENZYL MERCAPTAN (BM)

Benzyl Mercaptan is a useful raw material for making herbicides of different family like tiocarbazil, esprocarb, prosulfocarb, etc. (Labat, 1989). It was prepared by Hoffman and Reid in 1923 from BC and sodium sulfide in ethanolic solution at 90^0C. Then in 1988, it was synthesized by Heather via reacting BC with H_2S rich NaOH solution at 50^0C. Around 90% conversion was obtained after 5 hours of reaction at constant stirring.

It was also synthesized from BC and H_2S rich solution of ammonia and methanol at 0^0C. Complete conversion was obtained in 1 hour with 92% of BM selectivity (Bittell and Speier, 1978). Around 99% selectivity was noticed by Labat in 1989 by reacting BC with ammonium hydrosulfide with varying molar ratio of NH_4SH/BC in between 1.05 to 1.5 in closed reactor under pressure in two steps. First step involves mixing of reactant below 80^0C and in second step, reaction mixture was heated to 100^0C for 2 hours.

BM was also synthesized from thioacetates in presence of borohydride exchange resin methanolyzed for lead catalyst (Choi and Yoon, 1995a). Alkyl halides and epoxides were also used by Choi and Yoon in 1995b for BM synthesis in presence of hydrosulfide ion exchange resin and triethylammonium chloride.

2.2 DIBENZYL SULFIDE (DBS)

DBS is a useful fine chemical used in stabilizer in photographic emulsions, high pressure lubricants, additive as anti-wear in motor oil and has application in various anticorrosive formulations (Pradhan and Sharma, 1990). It is also become a raw material for synthesis of Dibenzyl sulfoxide and Dibenzyl sulfone after oxidation (Mohammadpoor - Baltorketetal., 2005).

Pradhan and Sharma in 1990 synthesized DBS and bis(p-chlorobenzyl) sulfide from chlorides and sodium sulfide under L-L and S-LPTC mode. Tetrabutylammonium bromide (TBAB) was obtained as most active catalyst compared to others. The reaction rate of BC with sodium sulfide was increased by Ido et al. in 2000 by converting biphasic PTC to insoluble PTC using Tetrahexylammonium bromide as a PTC.

Kinetic study of DBS was done by Pradhan and Sharma in 1992 using solid sodium sulfide in S-LPTC in presence of solid catalyst basic alumina and Amberlyst A27 (Cl^- form) anion exchange resin.

DBS was also synthesized from respective halides using sulfide anions supported on polymer (Bandgar et al., 2000) and by reducing respective disulfides in presence of Zn powder using $AlCl_3$ aqueous media (Lakouraj et al., 2002 ; Movassagh and Mossadegh, 2004a, 2004b). Reduction of sulfoxide using Al-$NiCl_2$-$6H_2O$ as reducing agents was also performed for synthesis of DBS (Raju et al., 2005). But due to long reaction time, expensive reagents and extreme reaction conditions, reduction is not an economical method (Iranpoor et al., 2002).

The use of PTC technique for DBS synthesis is also well documented. It was synthesized by Sen et al. in 2006 from BC and ammonium sulfide in L-LPTC using TBAB as PT catalyst. High DBS selectivity was noticed with high catalyst, ammonia and BC concentration at 50°C. Then Sen et al. in 2011 prepared DBS from H_2S rich MEA and BC and observed that MEA is good absorbent than ammonia and high concentration of MEA was required for high DBS selectivity.

2.3 DIBENZYL DISULFIDE (DBDS)

The use of sulfur transfer agent for DBDS synthesis is well documented in literature. Sulfurated borohydride exchange resin was used by Bandgar et al. in 2001 for disulfide synthesis from halides. It was prepared from alkyl halides from sulfur transfer agent Benzyl triethylammonium tetracosathioheptamolybdate under a very mild reaction condition (Polshettiwar et al., 2003). Then thiourea was used as a source of sulfur for disulfides synthesis from Primary, secondary, tertiary, allylic, and benzylic halides at 30-35°C using MnO_2 as an oxidizing agent in PEG-200 (Firouzabadi et al., 2010).

Oxidation of corresponding thiols to disulfides was also found as well accepted method. DBDS was synthesized from corresponding thiols to disulfides using 2,6-Dicarboxypyridinium chlorochromate as a reagent (Tajbakhsh et al., 2004). Disulfides was also synthesized from using microwave accelerates and 1-n-butyl-3-methylimidazolium methyl selenite (Thurow et al., 2011). Then a solid supported catalyst (Al_2O_3/KF) was used in solvent free condition for conversion of thiols to disulfide at room temperature (Lenardao et al., 2007). Oxidation of thiols to disulfides was done in presence of molecular bromine on solid support silica gel (Ali and McDermott, 2002). Easily recoverable supported iron oxide nanoparticles were used for DBDS synthesis using hydrogen peroxide as green oxidant for thiols (Rajabi et al., 2013).

Then PTC was used for synthesis of DBDS. Sonavane et al. in 2007 synthesized symmetrical disulfides sulfur with sodium sulfide using didecyldimethylammonium bromide as PT catalyst at room temperature.

2.4 PHASE TRANSFER CATALYSIS (PTC)

Yadav and Jadhav (2003) studied reduction of p-chloronitrobenzene with sodium sulfide in detail under the different mode of phase transfer catalysis such as (L-L), (L-S) and (L-L-L) processes. Role of co-catalyst in intensification of rate of L-L PT catalyzed reaction was also studied by them in allusion to synthesis of p-chlorophenyl acetonitrile by using TBAB as a PT catalyst and potassium iodide as a co-catalyst. Due to co-catalyst, 100% selectivity of product was obtained. Kinetics of reaction between benzyl bromide and sodium benzoate in L-L system catalyzed by Aliquat 336 at 70^0C for 3 h of reaction using chlorobenzene as a solvent was studied by Yang and Lin (2003). Product yield obtained was 98%.

Reduction of nitro toluene using an aqueous ammonium sulfide as a reducing agent was carried out in organic solvent toluene under L-LPTC in presence of TBAB. Selectivity of toluidines was found to be 100%. (Maity et al., 2006)

Wang and Lee (2007) studied kinetics of PTC etherification of 4,4´-bis(chloromethyl)-1,1´-biphenyl with phenol in alkaline solution of KOH/organic solvent as a two phase medium. Kinetics and mechanism of quaternary ammonium salt as a PT catalyst for oxidation of thiophene was observed by Zhao et al. (2007). Different catalyst with ultrasound was employed and quaternary ammonium salt was found to be best with 94.67% desulfurization rate.

So it can be concluded that PTC is a technique used to increase reactivity and selectivity of synthesis reactions where reactants are not soluble in one solvent. The migration of reactant from one phase to another is done by using a catalyst, called as phase transfer catalyst. Suitable catalyst is selected in the basis of nature of synthesis reaction, toxicity, activity, ease of preparation or availability and ease of recovery or recycle. In the present work, DBS and DBDS is prepared from BC and H_2S rich alkalonamine under L-L and L-L-S PTC respectively. Tetrabutylphosphonium bromide is selected as a PT catalyst for DBS synthesis whereas Amberlite IR-400 catalyst is used during DBDS synthesis.

CHAPTER 3

EXPERIMENTAL

3.1 CHEMICALS AND CATALYST

H_2S was produced in small scale using Kipp's apparatus and its absorbed sulfide concentration was estimated from Iodometric titration method. Chemicals like potassium iodate (KIO_3), potassium iodide (KI), sodium thiosulfate ($Na_2S_2O_3$), starch powder, 98% pure sulfuric acid (H_2SO_4) and pallets of sodium hydroxide (NaOH) were purchased from Merck (India) Ltd., Mumbai. The ferrous sulfide sticks (FeS) required in Kipp's apparatus was acquired from Sigma Aldrich, Mumbai, India. MEA and MDEA used as an absorbent were also obtained from Sigma Aldrich, Mumbai, India. The organic solvent toluene and reactant BC was bought from Merck (India) Ltd., Mumbai.

3.2 PREPARATION OF H_2S-RICH AQUEOUS ALKANOLAMINES

H_2S was prepared in small scale in laboratory in Kipp's apparatus by contacting FeS sticks with 1 M H_2SO_4 solution as shown in Fig. 3.1. H_2S generated was absorbed in to 30-35% aqueous alkanolamine in 250 ml slandered gas bubbler. The unabsorbed H_2S gas from bubbler was then send to the atmosphere.

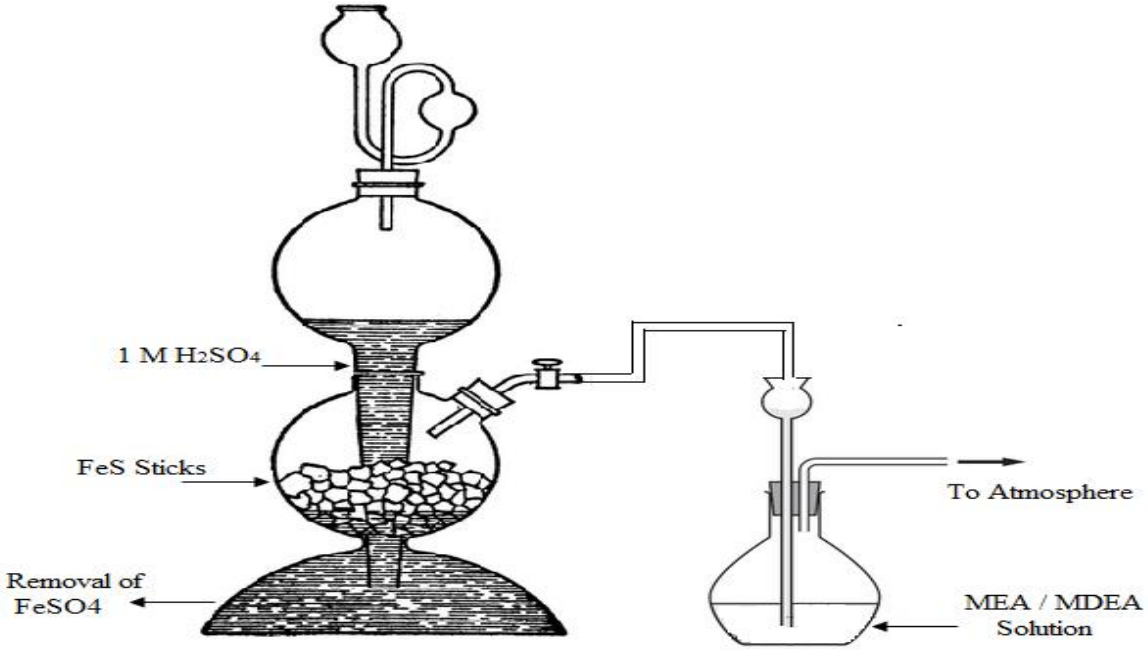


Figure 3.1: Schematic Diagram for Absorption of H_2S in MEA/MDEA Solution

The overall reaction is

$$Fes + H_2SO_4 \rightarrow H_2S + FeSO_4 \text{ (Exothermic)}$$

The $FeSO_4$ formed in reaction was taken out from the bottom of kipp's apparatus. Since the reaction is exothermic in nature (Kohl and Nielsen, 1997), the reagent bottles containing aqueous amine was kept in ice water bath to prevent oxidation of sulfide and formation of disulfide. Liquid samples were taken at different time interval after stopping gas bubbling and sulfide concentration was determined using Iodometric titration method (Scott, 1966). Continuous bubbling was done till required concentration of sulfide was obtained in aqueous alkanolamine.

3.3 IODOMETRIC TITRATION METHOD

The sulfide concentration of aqueous alkanolamine was determined by Iodometric titration method given by Scott in 1966.In this method, free iodine is liberated by reacting an oxidation agent in neutral or acidic medium with excess of potassium iodide (KI).

$$KI + \text{Oxidising Agent} \rightarrow I_2$$

A standard reducing agent usually with sodium thiosulphate is used to titrate liberated iodine. Starch solution is recommended as an indicator which shows free iodine liberation through blue or violet color. The complete change of iodine to iodide is identified with color change of blue to colorless. In present work, the steps followed were given below.

Preparation of standard 0.025 M KIO_3 solution: 5.35 gm of KIO_3 was dissolved in distilled water and was made up to 1 L in a graduated volumetric flask.

Preparation of standard 0.1 M sodium thiosulfate solution: $Na_2S_2O_3.5H_2O$ crystals of about 25 gm was added in distilled water and made up to 1 L in a graduated with distilled water. In order to keep the solution for few days, 0.1 g of sodium carbonate or three drops of chloroform was added to this solution.

Standardization of sodium thiosulfate solution by standard potassium iodate solution: 1 gm (excess) of potassium iodide KI was added in 25 mL of 0.025M KIO_3 solution followed by 3 mL of 1 M sulfuric acid. The liberated iodine was titrated with thiosulfate solution till color changes from brown to pale yellow. Then the solution was made up to 200 ml using distilled water and few drops of 0.2% iodine starch solution were added to it. After adding starch solution, the titration

was continued until color changes from blue to colorless. The starch solution was prepared by adding 0.2 g starch paste in 100 ml boiled water. Then solution was cooled and 2.5 gm of KI was added to make it 0.2% iodine starch solution. The chemical reaction involved in this titration is given below.

$$KIO_3 + 5KI + H_2SO_4 \leftrightarrow 3I_2 + 3H_2O + 3K_2SO_4$$

$$2Na_2S_2O_3 + I_2 \leftrightarrow Na_2S_4O_6 + 2NaI$$

Therefore, 1 mole of $KIO_3 \equiv 3\times2$ mole of $Na_2S_2O_3$.

$$\therefore \text{ Strenth of Thiosulfate Solution} = \frac{6 \times \text{Strenth of } KIO_3 \times \text{Volume of } KIO_3}{\text{Volume of Thiosulfate Consumed}}$$

Estimation of sulfide concentration: The phenomenon of oxidation of hydrogen sulfide and soluble sulfides with potassium iodate in an alkaline medium is used for sulfide estimation. Standard 0.025M potassium iodate solution of about 15cm^{3}was taken in a conical flask. 10 cm^3 of sulfide solution was then added to it followed by addition of 10 cm^3 of 10M sodium hydroxide solution. The resulting mixture was then boiled for about 10 minutes. After cooling, 5 cm^3 of 5% KI solution and 20 cm^3 of 4M sulfuric acid solution were added to it. The liberated iodine was titrated with 0.1M sodium thiosulfate in the usual manner. The oxidation of sulfide to sulfate by potassium iodate in the alkaline medium is given by reaction below.

$$4IO_3^- + 6OH^- + S^{2-} \rightarrow 4SO_4^{2-} + 4I^- + 6H_2O$$

$$4 \text{ moles of } IO_3^- = 3 \text{ moles of } S^{2-}$$

$$\therefore H_2S \text{ Concentration} = \left[15 \times S_{iodate} - \frac{V_{thiosulfate} \times S_{thiosulfate}}{6}\right] \times \frac{3}{4} \times \frac{N_d}{10}$$

Where, S_{iodate} = Strength of KIO_3

$V_{thiosulfate}$ = Volume of thiosulfate

$S_{thiosulfate}$ = Strength of thiosulfate

N_d = Number of times of dilution

3.4 APPARATUS AND EQUIPMENT SETUP

The experiment was performed in a thermostated three necked 250 ml baffled mechanically agitated glass batch reactor. A six blade glass turbine impeller with facility of speed regulation was used for stirring the reaction mixture. The impeller was placed at the height of 1.5 cm from bottom. The whole reaction assembly was then kept in a water bath. The temperature of water bath could be controlled within $\pm 0.5^0$C. The complete assembly of experimental setup is shown in Fig. 3.2.

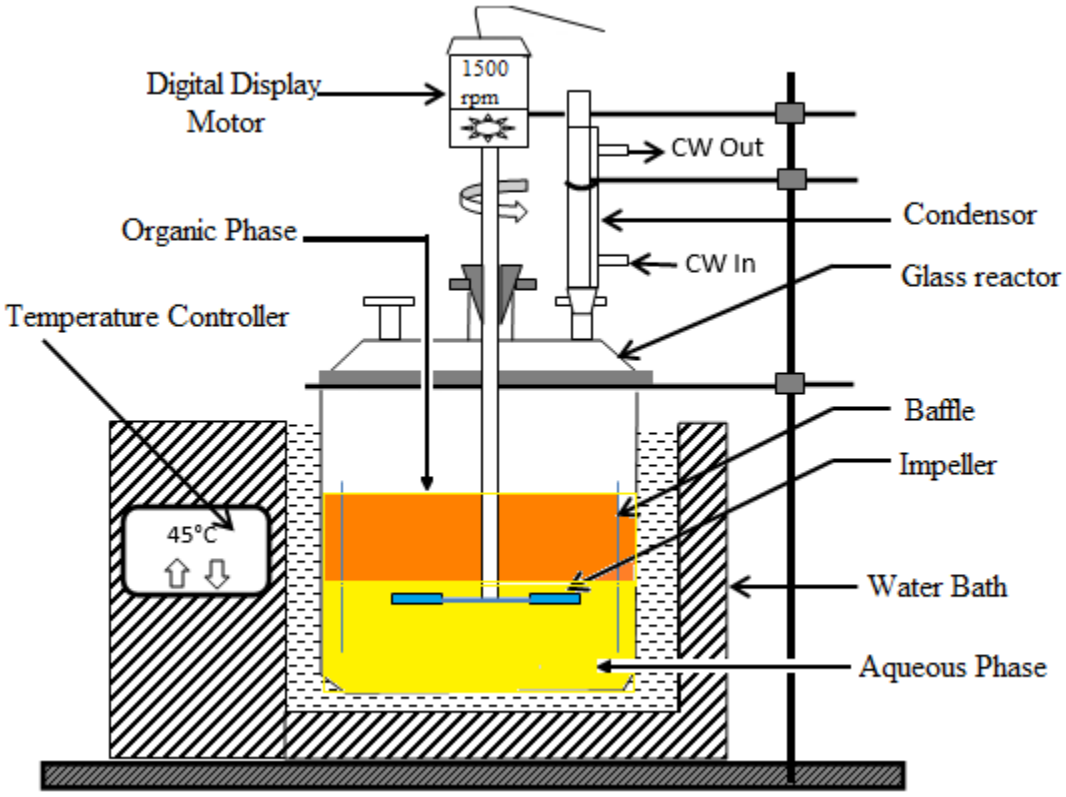


Figure 3.2: Batch Reactor Assembly

3.5 EXPERIMENTAL PROCEDURE

First 50 ml H_2S rich aqueous MEA/MDEA solution prepared in Kipp's apparatus was taken and charged in a batch reactor assembly as shown in Fig. 3.2 and vigorously agitated to reach a steady state reaction temperature. After that, 50 ml solution of solvent toluene and organic reactant BC along with PT catalyst (Amberlite-400/ TBPB) was charged in batch reactor containing aqueous phase. Then to start the reaction, reactor mixture was agitated constantly. Reaction sample

of around 1ml was taken from organic phase at regular interval of time. For this, first reaction agitation was stopped and aqueous and organic phase were allowed to settle down so that clearly visible organic phase will form above the aqueous phase. The organic sample was collected in sample bottle and analyzed using gas chromatography (GC).

3.6 ANALYSIS OF ORGANIC PHASE

The concentration of Benzyl mercaptan (BM), Dibenzyl sulfide (DBS) and Dibenzyl disulfide (DBDS) dissolved in organic phase was evaluated using gas liquid chromatography (GLC). GC is an analytical technique used in industrial laboratory for identification and measurement of quantity of compounds present in a mixture. Gas –Liquid chromatography generally known as GC contains gas as a mobile phase and liquid as a stationary phase. Carrier gas is generally an inert gas like helium or unreactive gas like nitrogen. Stationary phase is a very thin (microscopic) layer of liquid coated on surface of column.

In GC, a known amount of sample is first injected by a micro-syringe on to the head of chromatographic column with carrier gas as shown in Fig. 3.3 below. Sample travels with carrier gas through column coated with stationary phase. In column, interaction between sample component and stationary phase takes place and hence, different component elute at different retention time from column depending on their interaction with stationary phase. A detector is placed at the outlet of column to determine retention time and amount of components leaving the column.

The commonly used detector for organic components is a Flame Ionization Detector (FID). Electrodes are placed just outside the column with burning fuel air/ hydrogen. When the organic compounds exist from the column, it is pyrolyzed by the flame. Carbon compound produces cations and electrons during pyrolysis and current is generated between the electrodes. The generated current singles are transported and appears in the form of peaks on the graph called as chromatogram.

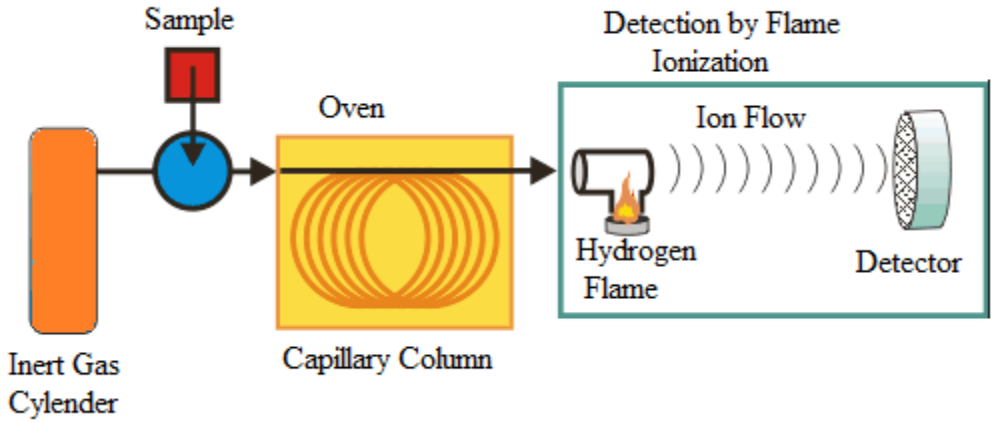


Figure 3.3: Assembly of Gas Chromatography with FID Detector

In present work, GC-MS from Agilent Technology of model 7890B was used with FID detector. MS was used for identification and FID detector was used for quantitative measurement of compound of organic sample. Program for MS and FID was evaluated given below:

MS PROGRAM

Injection Volume = 1µl

Inlet

Heater = 300^0C

Pressure = 11.724 psi

Purge Flow = 3ml/min

Mode = Split less

Column

Agilent DB-5ms

Flow = 1 ml/min

Pressure = 8.2317 psi

Holdup Time = 1.365 min

Oven

Oven Temperature = 60^0C

Maximum Oven Temperature = 324^0C

	Rate (^{0}C/min)	Value (^{0}C)	Holdup Time (min)	Retention Time (min)
Initial		60	0.25	0.25
Ramp 1	100	150	0	1.15
Ramp 2	50	300	5	9.15

FID PROGRAM

Injection Volume = 1µl

Inlet

Heater = 200^{0}C

Pressure = 15.345 psi

Purge Flow = 3ml/min

Column

Agilent DB-5ms

Flow = 1.5 ml/min

Pressure = 15.345 psi

Holdup Time = 1.427 min

Oven

Oven Temperature = 60^{0}C

Maximum Oven Temperature = 324^{0}C

	Rate (^{0}C/min)	Value (^{0}C)	Holdup Time (min)	Retention Time (min)
Initial		50	0	0
Ramp 1	30	170	0	4
Ramp 2	50	260	0	5.8
Ramp 3	10	280	1.2	9

Detector

Heater = 300^0C

Air Flow = 400 ml/min

H_2 Flow = 30 ml/min

Make up Flow (N_2) = 25 ml/min

Column Flow (N_2) = 15 ml/min

The chromatogram of DBDS system for 5min and 480min are shown in Fig. 3.4 and 3.5 respectively. From the chromatogram, it is clear that toluene is not participating in synthesis reaction and act as a solvent. No appearance of BC in 480 min shows complete conversion of reactant and consequently increase in product concentration.

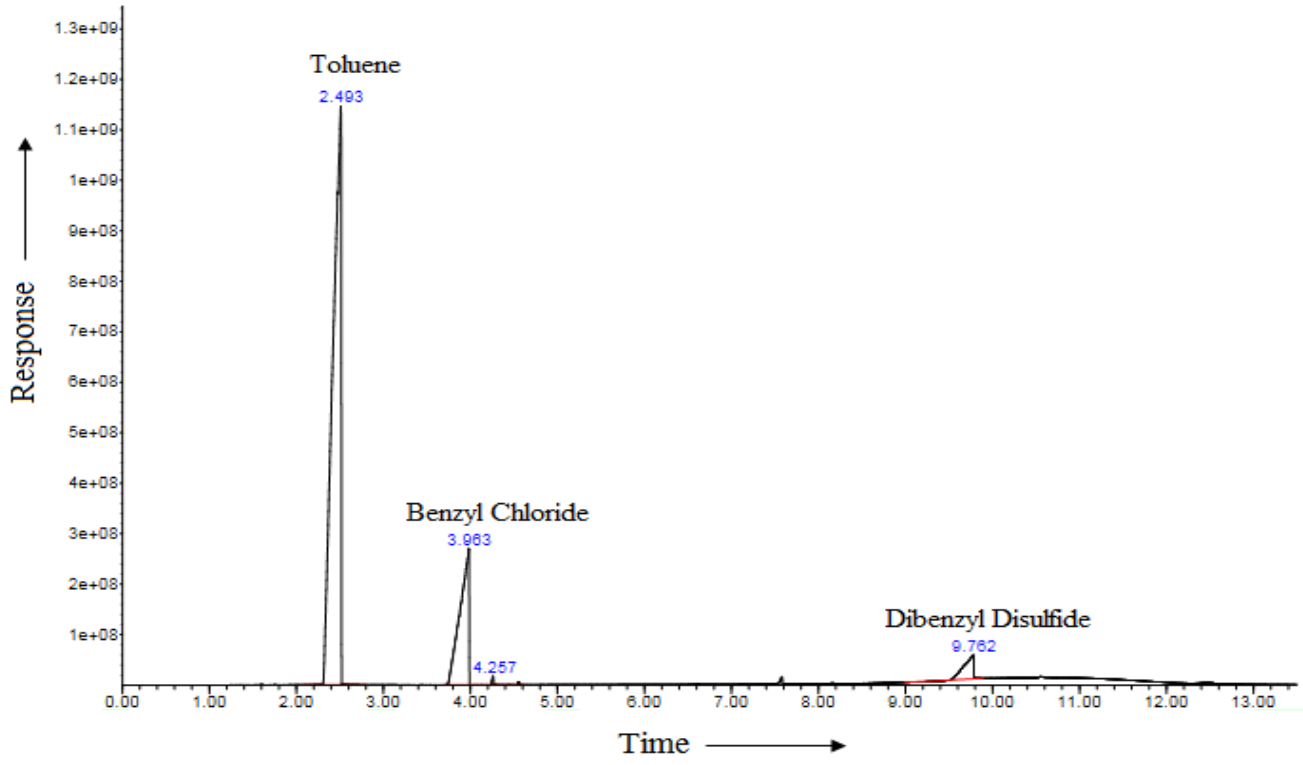


Figure 3.4: Chromatogram of DBDS Synthesis in 5 min

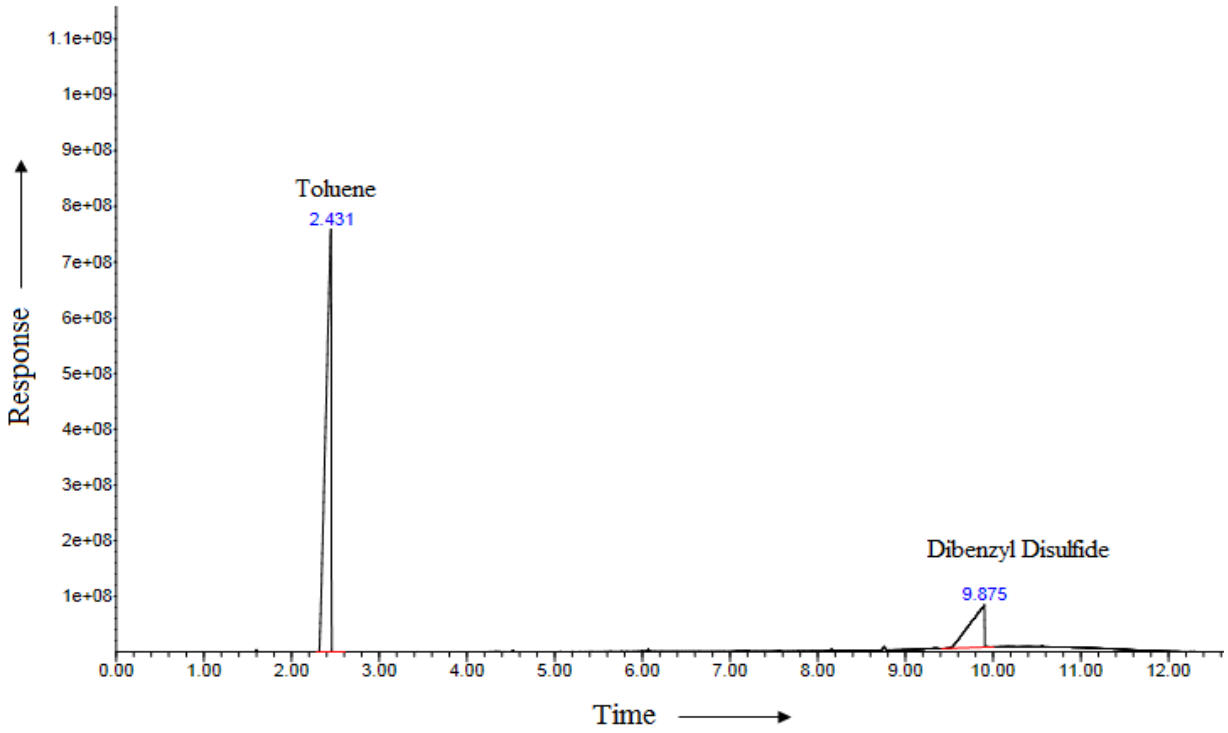
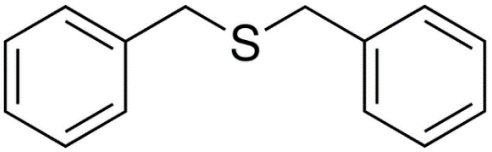


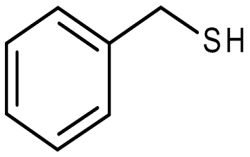
Figure 3.5: Chromatogram of DBDS Synthesis in 480 min

CHAPTER 4

SYNTHESIS OF DIBENZYL SULFIDE (DBS) AND BENZYL MERCAPTAN (BM)



DBS

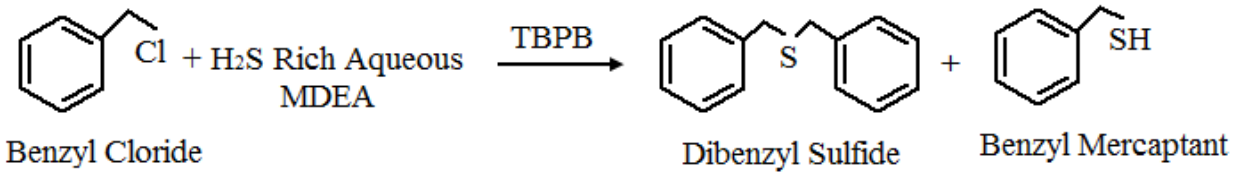


BM

4.1 INTRODUCTION

In present work, value added chemicals like Dibenzyl sulfide (DBS) and Benzyl mercaptan (BM) was synthesized from BC dissolved in toluene and H_2S rich aqueous MDEA in batch reactor under L-LPTC in presence of Tetrabutylphosphonium Bromide (TBPB) as a PT catalyst. DBS is a white solid crystal or powder having an unpleasant smell. It has various industrial applications like additives for extreme pressure lubricants, anti-wear additives for motor oils, stabilizers for photographic emulsions, in refining and recovery of precious metals, and in different anti-corrosive formulations. Benzyl mercaptant finds application in synthesis of herbicides like esprocarb, prosulfocarb, tiocarbazil etc (Sen et al., 2010).

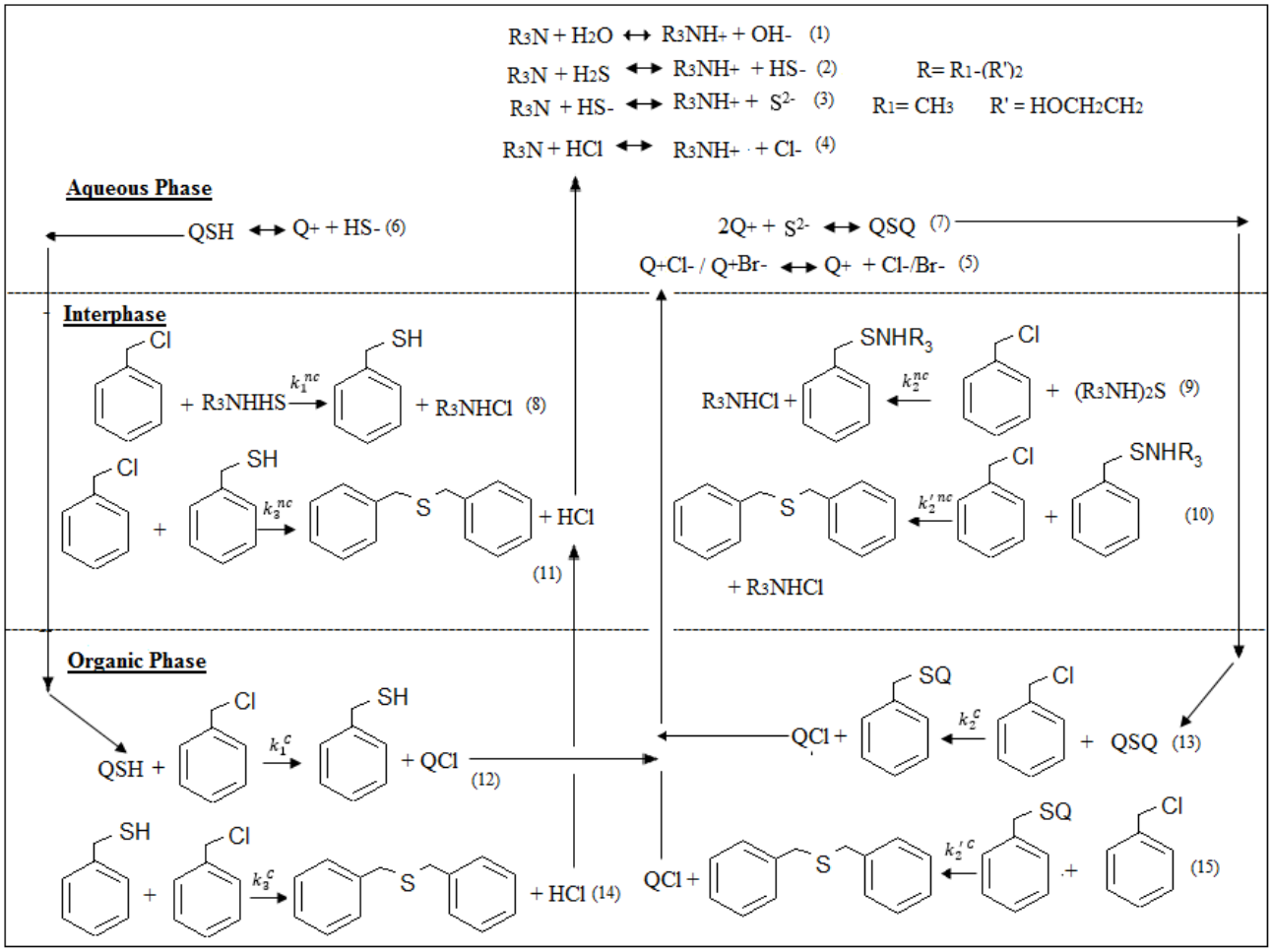
The products concentration was detected using gas-liquid chromatography (GLC). Reaction parameters for increasing selectivity and conversion of reactant were studied. The unwanted side reaction of hydrolysis of BC was not detected even after 10 hours of reaction time. The overall reaction is represented in Scheme 4.1.



Scheme 4.1

4.2 MECHANISTIC INVESTIGATION

The mechanism of L-LPTC can be explained either by extraction mechanism or by interfacial mechanism based on lipophilicity of catalyst. The extraction mechanism suggested by Starks (1971) and Starks and Liotta (1978), is useful if catalyst is having good distribution coefficient between aqueous and organic phase. In interfacial mechanism, catalyst is too lipophilic in nature that it entirely remains in organic phase and ion exchange reaction takes place in aqueous organic interphase. But in present situation, TBPB can distribute itself between aqueous and organic phase so that ion exchange reaction takes place in aqueous phase and nucleophilic substitution reaction takes place in organic phase. So the mechanism is explained by stark's extraction mechanism in Scheme 4.2 below.



Scheme 4.2

Generally aqueous phase reactions are faster compare to organic phase reactions, so an ionic equilibrium exists in aqueous phase between R_3N (MDEA)-H_2O-H_2S which results in formation of three active inorganic nucleophiles namely hydroxide $(OH)^-$, hydrosulfide (HS^-) and sulfide (S^{2-}) represented by equation 1-4. These ions are capable of reacting with quaternary phosphonium cation Q^+ $[(C_4H_9)_4\ P^+]$ to produce QOH, QSH and QSQ ion pairs in aqueous phase. Since TBPB is having good partition coefficient, these ion pairs transfers from aqueous phase to organic phase where they react with organic reactant to give desired product. However, the unwanted side products of hydrolysis from reaction between QOH ion pair and BC like benzyl alcohol ($C_6H_5CH_2OH$) or benzyl amine ($C_6H_5CH_2NH_2$) were not identified in GLC. This is due to fact that QOH ion pair is too hydrophilic in nature that can't easily transfer to organic phase (Wang

and Tseng, 2003). The reaction product was obtained due to contribution of both catalytic and non-catalytic reactions.

4.2.1. Non-catalytic Contribution: Methyldiethanolamine hydrosulfide (R_3NHHS) and sulfide $(R_3NH)_2S$ formed in an aqueous phase are insoluble in organic phase so they are expected to react with BC at aqueous-organic interface to yield BM and DBS respectively. The non-catalytic reactions of interface are represented by equations 8-11. Since nucleophilic substitution reactions are generally 2nd order, so reaction between BC and $(R_3NH)_2S$ are assumed to form an intermediate $C_6H_5CH_2SNHR_3$ which further react with BC to produce DBS. Some BM again reacts with BC to give high selectivity of DBS.

4.2.2. Catalytic Contribution: The transferred catalyst ions pairs QSQ and QSH in organic phase react with organic reactant BC to give BM and DBS respectively shown in equations (12-15). Again DBS was synthesized via formation of intermediate product $C_6H_5CH_2SQ$ which further reacts with BC to give desired product DBS. Both the intermediate formed in interface and organic phase were not identified by GLC. Fig 4.1below shows the concentration profile of a batch reactor.

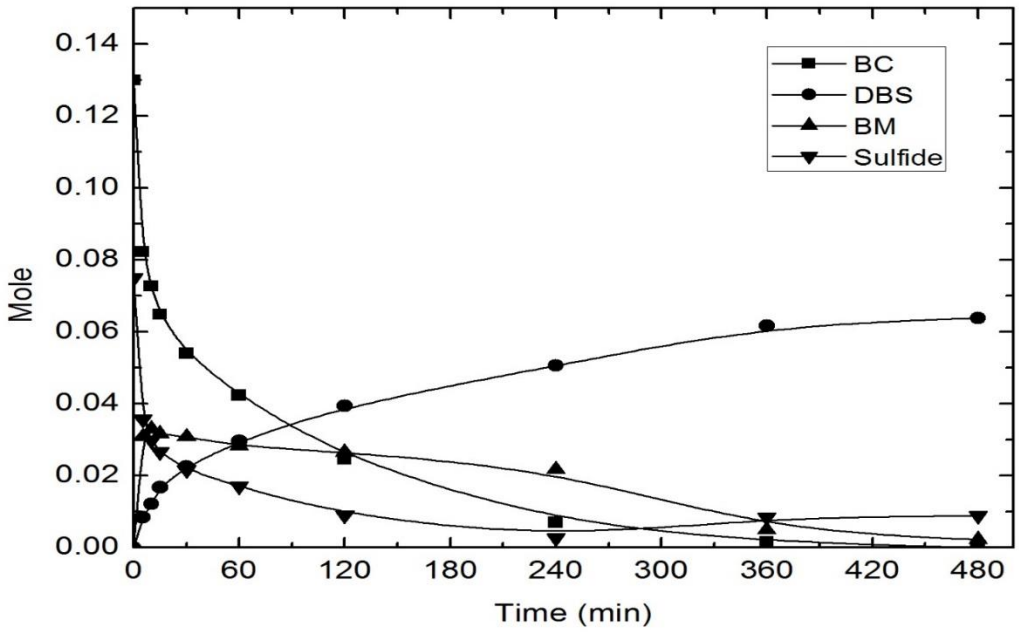


Figure 4.1: Typical Concentration Profile for DBS Synthesis

From the concentration profile, it is observed that BM first reaches its maximum concentration and then gradually decreases with time. So it is concluded that BM reacts with BC

to give high selectivity of DBS and produces hydrochloric acid (HCl). But this reaction is expected to be slow since a strong HCl acid is formed from weak BM acid.

4.3. MATHEMATICAL MODELING

The overall rate of reactions from both non-catalytic and catalytic contribution are given as follows ($C_6H_5CH_2$-=**R**):

$$\left|\frac{d[\mathbf{R}X]}{dx}\right|_{overall} = \left|\frac{d[\mathbf{R}X]}{dx}\right|_{non-catalytic} + \left|\frac{d[\mathbf{R}X]}{dx}\right|_{catalytic} \quad (4.1)$$

$$\left|\frac{d[\mathbf{R}SH]}{dx}\right|_{overall} = \left|\frac{d[\mathbf{R}SH]}{dx}\right|_{non-catalytic} + \left|\frac{d[\mathbf{R}SH]}{dx}\right|_{catalytic} \quad (4.2)$$

$$\left|\frac{d[\mathbf{R}S\mathbf{R}]}{dx}\right|_{overall} = \left|\frac{d[\mathbf{R}S\mathbf{R}]}{dx}\right|_{non-catalytic} + \left|\frac{d[\mathbf{R}S\mathbf{R}]}{dx}\right|_{catalytic} \quad (4.3)$$

The net rate of formation of product in the absence of catalyst through non-catalytic reactions are given below:

$$\left|\frac{d[\mathbf{R}X]}{dt}\right|_{non-catalytic} = (-k_1^{nc}[R_3NHSH] - k_2^{nc}[(R_3NH)_2S] - k_2^{nc}[\mathbf{R}SNHR_3] - k_3^{nc}[\mathbf{R}SH])[\mathbf{R}X] \quad (4.4)$$

$$\left|\frac{d[\mathbf{R}SH]}{dt}\right|_{non-catalytic} = k_1^{nc}[\mathbf{R}X][R_3NHSH] - k_3^{nc}[\mathbf{R}X][\mathbf{R}SH] \quad (4.5)$$

$$\left|\frac{d[\mathbf{R}S\mathbf{R}]}{dt}\right|_{non-catalytic} = k_2'^{nc}[\mathbf{R}\mathbf{X}][\mathbf{R}SNHR_3] + k_3^{nc}[\mathbf{R}X][\mathbf{R}SH] \quad (4.6)$$

In the presence of PTC, reaction follows both catalytic and non-catalytic pathway. The equations 12-15 from the reaction mechanism represents catalytic pathway. Like a non-catalytic pathway, reaction between BC with QSQ is also assumed to proceed with formation of an intermediate RSQ. Rate of formation is given by

$$\frac{d[\mathbf{R}SQ]}{dt} = k_2^c[\mathbf{R}X][QSQ]_o - k_2'^c[\mathbf{R}X][\mathbf{R}SQ] \quad (4.7)$$

But the formation of RSQ was not identified in GL analysis, therefore concentration of RSQ is assumed to proceed through pseudo steady state hypothesis given by

$$[\mathbf{R}SQ] = \frac{k_2^c[QSQ]_o}{k_2'^c} \quad (4.8)$$

The rate of formation of BC, BM and DBS through catalytic pathway are represented by following equations. The RSQ concentration is replaced by equation 4.7.

$$\left|\frac{d[\mathbf{R}X]}{dt}\right|_{catalytic} = -k_1^c[\mathbf{R}X][QSH]_o - k_2^c[\mathbf{R}X][QSQ]_o - k_2'^c[\mathbf{R}X][\mathbf{R}SQ]_o - k_3^c[\mathbf{R}X][\mathbf{R}SH] \quad (4.9)$$

$$\left|\frac{d[\mathbf{R}SH]}{dt}\right|_{catalytic} = k_1^c[\mathbf{R}X][QSH]_o - k_3^c[\mathbf{R}X][\mathbf{R}SH] \quad (4.10)$$

$$\left|\frac{d[\mathbf{R}S\mathbf{R}]}{dt}\right|_{catalytic} = k_2'^c[\mathbf{R}X][\mathbf{R}SQ]_o + k_3^c[\mathbf{R}X][\mathbf{R}SH] \quad (4.11)$$

4.3.1 Modeling of Aqueous Phase Ionic Equilibria

A good thermodynamic framework of vapor- liquid equilibrium for aqueous solutions containing one or more volatile weak electrolytes: NH_3, CO_2, H_2S, SO_2, and HCN was developed by Edwards et al. (1975). With reference to this, an ionic equilibrium framework of R_3N-H_2O-H_2S is developed in present work for aqueous phase. This ionic equilibrium gives seven species in aqueous phase namely R_3N, H_2S,$[R_3NH^+]$, H^+, HS^-, S^{2-} and OH^-. The ionic equilibrium is expressed by dissociation constant in terms of their molar concentration in aqueous phase, can be obtained easily from literature (Bard, 1966), represented in equation 4.12- 4.15.

$$K_{R_3N} = \frac{[R_3NH^+][OH^-]}{[R_3N]} \quad (4.12)$$

$$K_{H_2S} = \frac{[HS^-][H^+]}{[H_2S]} \quad (4.13)$$

$$K_{HS^-} = \frac{[S^{2-}][H^+]}{[HS^-]} \quad (4.14)$$

The ion product constant of water is given as

$$K_{H_2O} = [OH^-][H^+] \quad (4.15)$$

To get concentration of seven species, we need three more equation in addition to above equations. So mass balance and charge balances are taken.

Total MDEA balance in aqueous phase

$$T_{R_3N} = [R_3NH^+] + [R_3N] \quad (4.16)$$

Total sulfide balance in aqueous phase

$$T_S = [HS^-] + [H_2S] + [S^{2-}] \quad (4.17)$$

Concentration of Charged species in aqueous phase is given as (from Eq. (1), (2) and (3))

$$3\,[R_3NH^+] + [S^{2-}] - [OH^-] = 0 \quad (4.18)$$

Now to find out ions concentrations, we have 7 unknowns and 7 equations sated above, can be easily solved in MATLAB SOFTWARE as linear simultaneous algebraic equations. The concentration of different sulfur species at 25^0C were calculated by varying total MDEA and H_2S concentrations.

From the simulation, it was seen that hydrosulfide ions are the controlling sulfur species at high total sulfide concentration and its concentration increases with increase total sulfide concentration in the aqueous phase at constant MDEA concentration shown in Fig 4.2. Whereas high MDEA concentration gave high sulfide ion concentration than hydrosulfide ion concentration shown in Fig 4.3. From this result, it may be concluded that at high MDEA concentration, the dissociation equilibria of reactions 1-4 of Scheme 4.2 shift towards right giving more sulfide ion (S^{2-}) than hydrosulfide ion (HS^-).

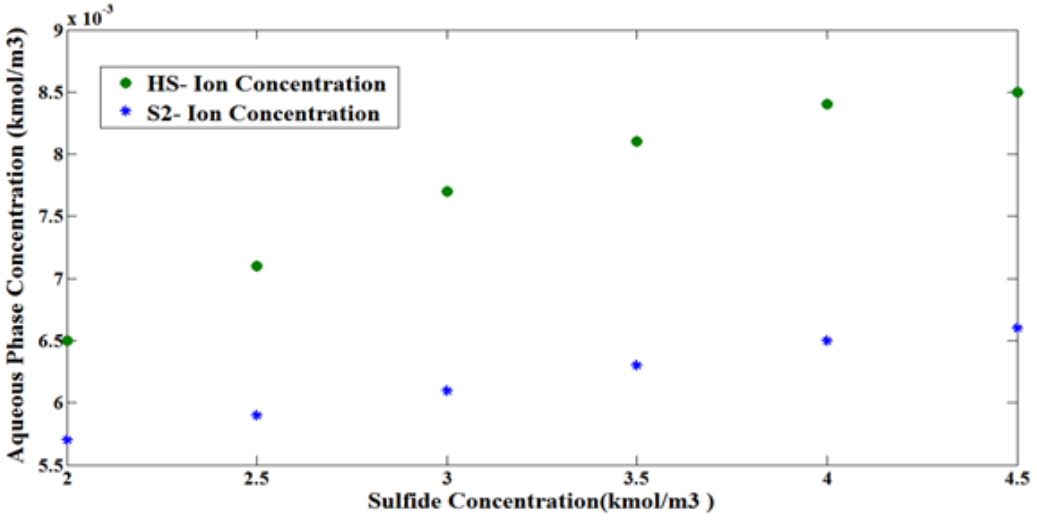


Figure 4.2: Effect on HS^- and S^{2-} Ions Concentration in Aqueous Phase with Increase in Sulfide Concentration at Constant Total MDEA Concentration of 5 kmol/m^3

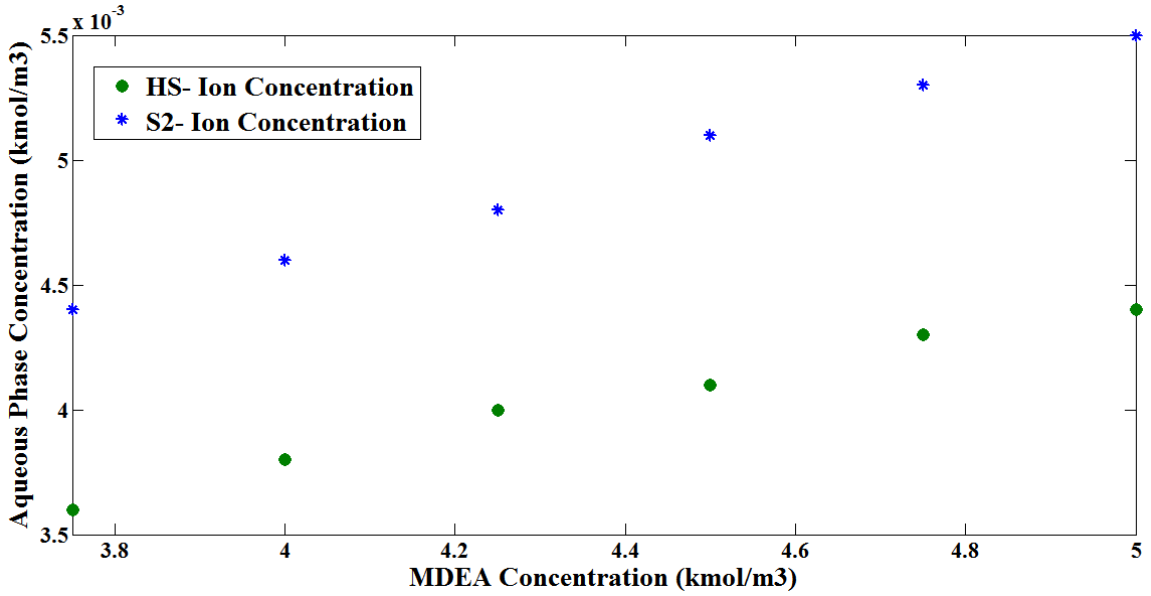


Figure 4.3: Effect of HS^- and S^{2-} Ions Concentration in Aqueous Phase with Increase in MDEA Concentration at Constant Total Sulfide Concentration of 1 kmol/m^3

4.3.2. Modeling of Catalyst Intermediate

TBPB is not too lipophilic in nature. So it can distribute itself between aqueous and organic phase. The dissociation equilibrium constants of PTC (QX) and active intermediates QSQ and QSH in aqueous phase are given by

$$K_{QX} = \frac{[Q^+][X^-]}{[QX]_a} \tag{4.19}$$

$$K_{QSH} = \frac{[Q^+][HS^-]}{[QSH]_a} \tag{4.20}$$

$$K_{QSQ} = \frac{[Q^+]^2[S^{2-}]}{[QSQ]_a} \tag{4.21}$$

The equilibrium distribution coefficient for PTC and active intermediates are defines as follows:

$$m_{QX} = \frac{[QX]_o}{[QX]_a} \tag{4.22}$$

$$m_{QSH} = \frac{[QSH]_o}{[QSH]_a} \tag{4.23}$$

$$m_{QSQ} = \frac{[QSQ]_o}{[QSQ]_a} \tag{4.24}$$

At any instant of time, the total sulfide concentration $[T_s]$ in aqueous phase expressed in kmol/m^3 is given by the sum of the sulfides present in both aqueous and organic phase. In aqueous phase, sulfide is present in the form of molecular sulfur specie (H_2S) and ionic sulfur species (HS^- and S^{2-}). Whereas it forms an active catalyst intermediates (QSH and QSQ) in organic phase.

$$T_s = [H_2S] + [HS^-] + [S^{2-}] + [QSQ]_a + [QSH]_a + \frac{V_o}{V_a}([QSH]_o + [QSQ]_o) \tag{4.25}$$

Simillarly, total initial catalyst concentration added in reaction mixture $[Q_0]$ is the sum of PTC in aqueous phase in form of molecular, ionic and active catalyst and in form of molecular and active catalyst in organic phase represented as

$$Q_0 = [QX]_o + [QSH]_o + 2 * [QSQ]_o + \frac{V_a}{V_o}([Q^+] + [QX]_a + [QSH]_a + 2 * [QSQ]_a) \tag{4.26}$$

From the reaction mechanism, it is clear that to get high selectivity of DBS, concentration of QSQ catalyst intermediate should be higher than QSH. These catalyst intermediate concentrations in aqueous and organic phase are calculated by solving equations 4.19-4.26 using MATLAB SOFTWARE as linear simultaneous algebraic equations to find out the effect of different patameters on production of catalyst intermediates and selectivity of DBS.

The required quantity of catalyst $[Q_0]$ is added to system and concentration of $[HS^-]$ and $[S^{2-}]$ ions are obtained from modeling of aqueous phase ionic equellibrium. The values of dissociation equilibrium constants and equilibrium distribution coefficients are taken from the work of Wu et al., 1998 for the system water/ chlorobenzene since this system closely resembles the present work.

4.3.2.1. Effect of MDEA Concentration

It is found that at adequate constant concentration of initial catalyst and total sulfur added, the concentration of [QSQ] intermediates are higher than [QSH] in both aqueous and organic phase

at high total MDEA concentration, shown in Fig 4.4 below, giving high selectivity of DBS according to reactions 13 and 14 of reaction mechanism.

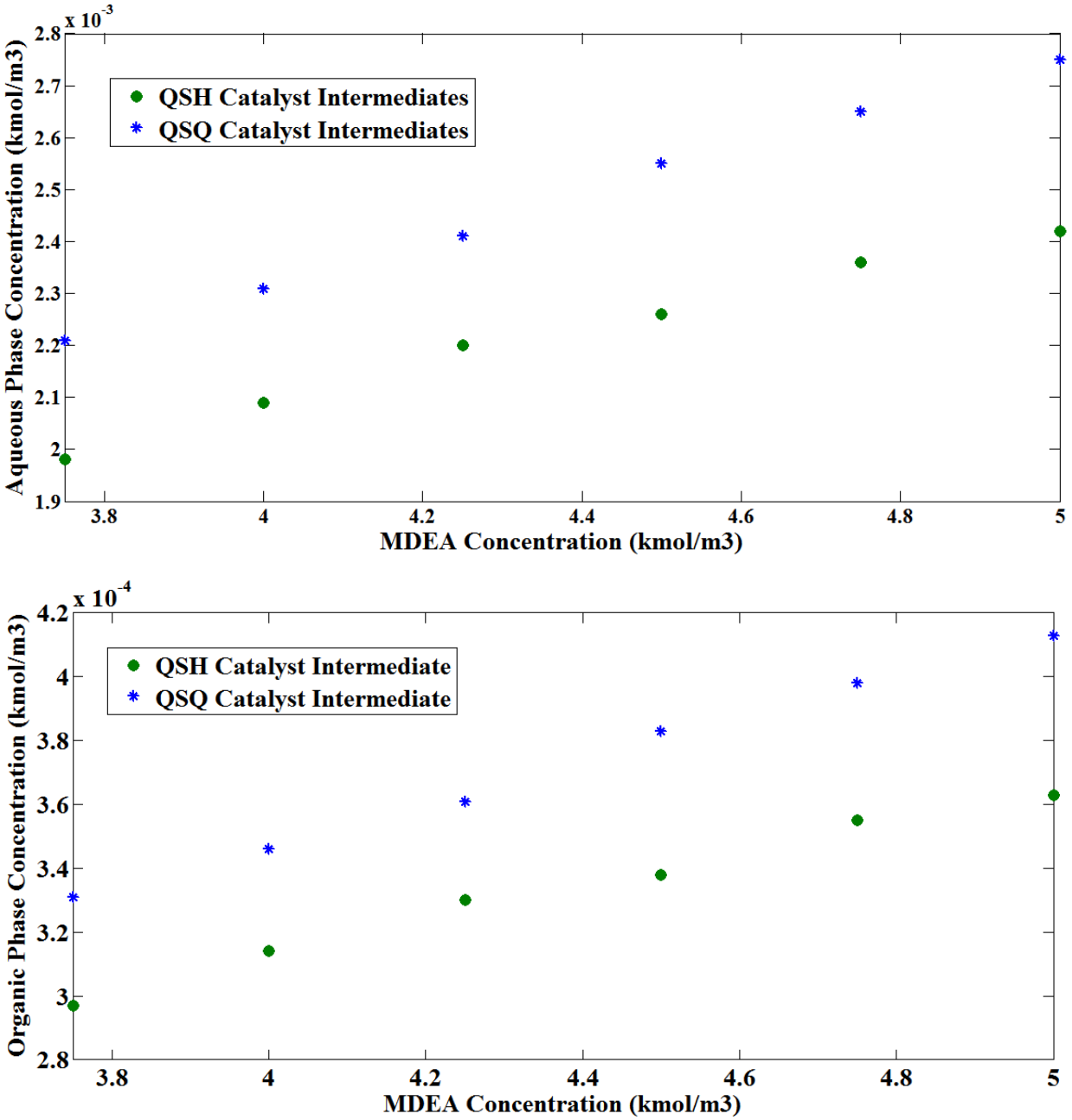


Figure 4.4: Effect of MDEA Concentration on Catalyst Intermediate; Ts= 1kmol/m^3 and Q_0=1.5 kmol/m^3

4.3.2.2. Effect of Sulfide Concentration

The opposite trend is observed with high concentration of sulfur, shown in Fig. 4.5 below, giving high yield of benzyl mercaptan than DBS. So selectivity of DBS and formation of QSQ catalyst is found to decreases with increase in total sulfur concentration.

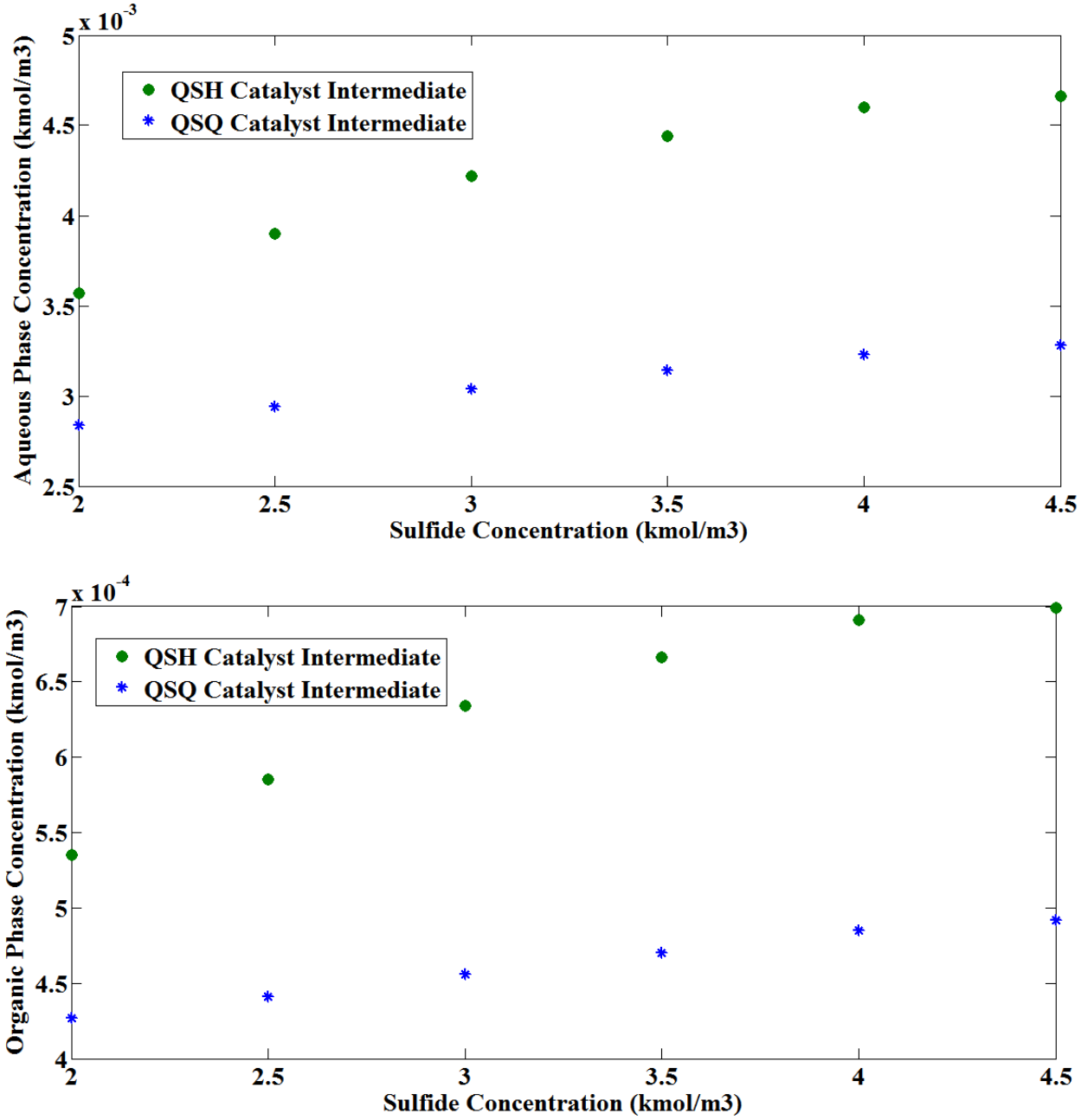


Figure 4.5: Effect of Sulfur Concentration on Catalyst Intermediate; T_{MDEA}= 5 kmol/m^3 and Q_0= 1.5 kmol/m^3

4.3.2.3. Effect of Catalyst Concentration

With increase in catalyst concentration, more amount of [QSQ] ion pairs are formed and transferred to the organic phase and reacts with benzyl chloride to form DBS. The selectivity of DBS, therefore, increases with increase in catalyst concentration shown in Fig. 4.6.

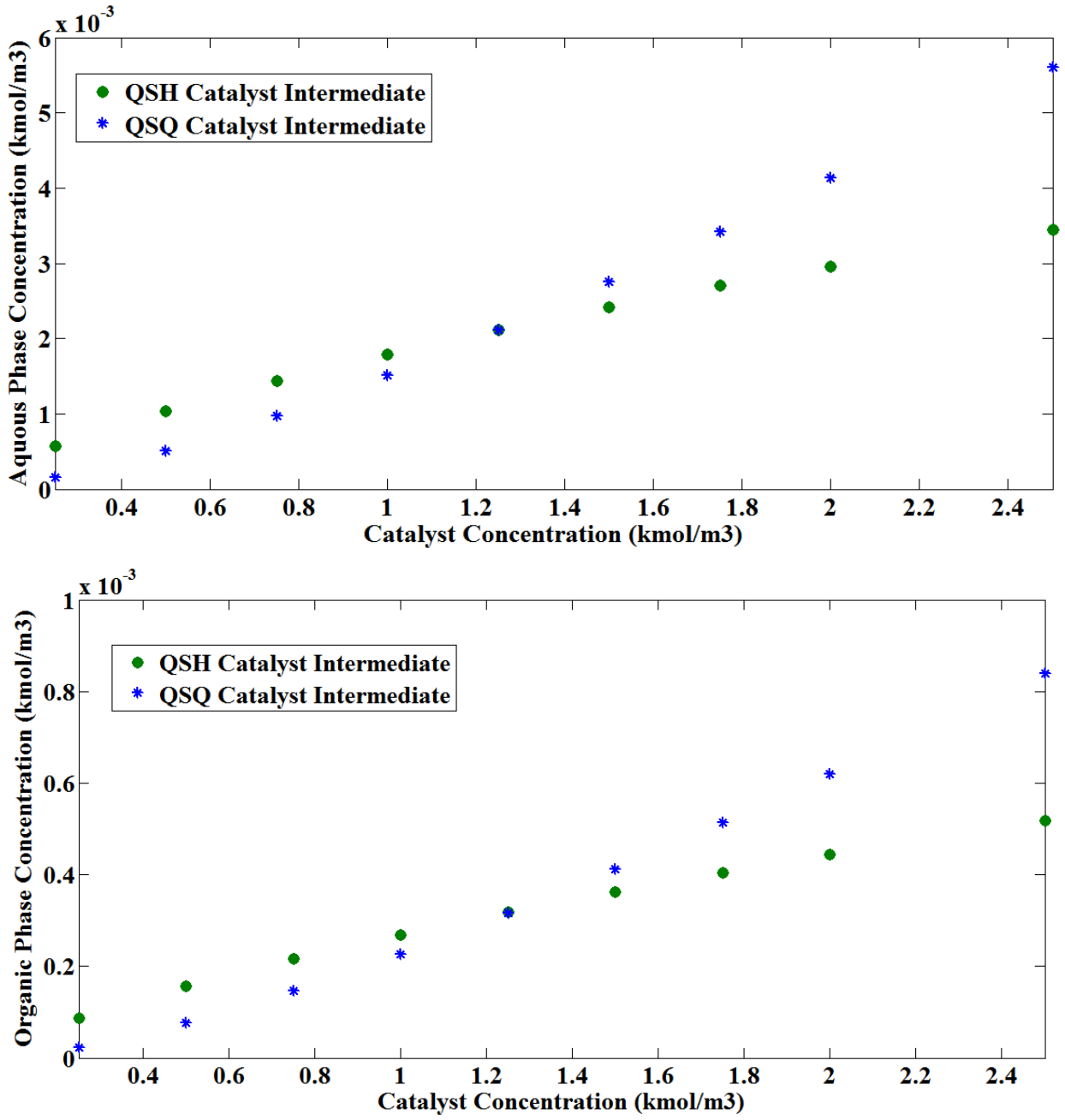


Figure 4.6: Effect of Catalyst Concentration on Catalyst Intermediate; T_{MDEA}= 5 kmol/m^3 and Ts = 1 kmol/m^3

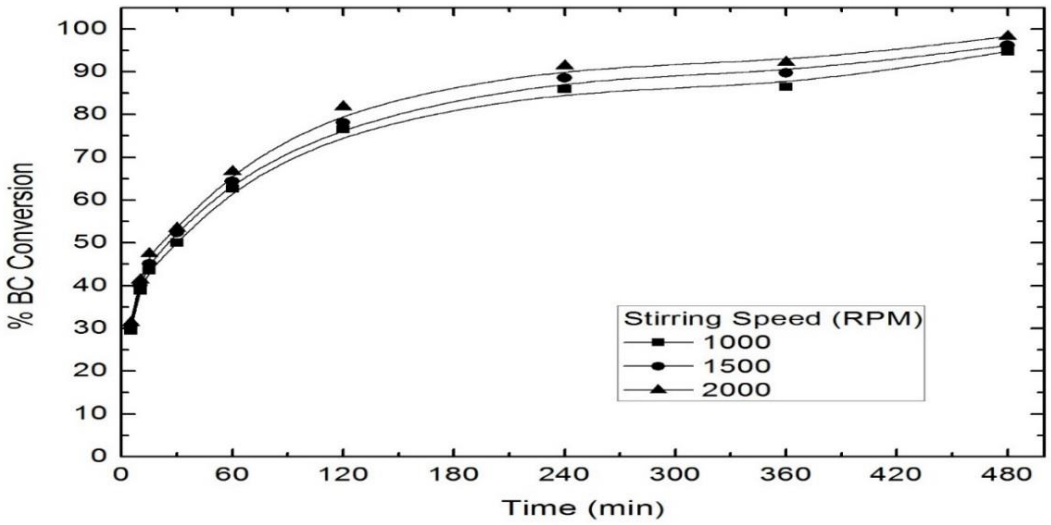
From modeling of aqueous phase equilibrium and catalyst intermediates, it was noticed that high catalyst and MDEA concentration increases sulfide ions in aqueous phase which is responsible for QSQ catalyst active intermediate production in both aqueous and organic phase. So increased DBS selectivity is expected at high catalyst and MDEA concentration according to reaction 13 and 14 of Scheme 4.2. The opposite trend was observed with high sulfide concentration in aqueous phase, giving high concentration of hydrosulfide ions than sulfide ions in aqueous phase for QSH catalyst intermediate production. So decrease in DBS selectivity is expected according to reaction 12 of Scheme 4.2.

4.4. EFFECT OF REACTION PARAMETER

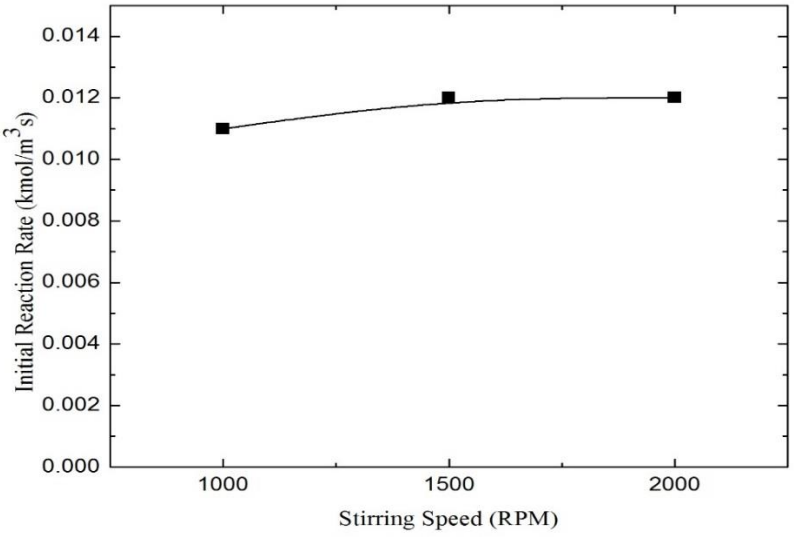
The reaction between BC in organic phase and H_2S rich MDEA is carried out at different reaction conditions to increase complete conversion of BC and selective synthesis of desired product DBS. This study also helps in decreasing reactor volume and development of profitable and cost effective method of product synthesis. This study is also important for reducing loss of solvent, catalyst and reactants and also increases the safety of synthesis process.

4.4.1 Effect of Stirring Speed

To determine the effect of mass transfer barrier on synthesis reaction, stirring speed in range of 1000-2000 RPM was varied keeping other reaction conditions same in presence of TBPB as a PT catalyst under L-L PTC condition as shown in Fig. 4.7 (a)below. The conversion was almost same indicating that reaction mechanism is free from mass transfer resistance. Initial reaction rate at 5% conversion was also checked with this range of stirring speed (Fig. 4.7 (b)). Nearly same initial rate of reaction was noticed. So from above discussion, it is concluded that reaction is fully kinetically controlled and mass transfer resistance factor is insignificant in nature. So 1500 RPM is consider as an optimum reaction parameter and further experiments are conducted with this stirring speed.



(a)



(b)

Figure 4.7: Influence of agitation speed on (a) BC conversion (b) Initial Reaction Rate Aqueous and Organic Phase Volume = 50 × 10^{-5}m^3 each, Sulfide Conc. = 1.5 kmol/m^{3}Aqu. Phase, BC moles = 0.261 mol, TBPB = 0.1 kmol/m^3 org. phase, Temperature = 323K, MDEA Conc. = 3.05 kmol/m^3

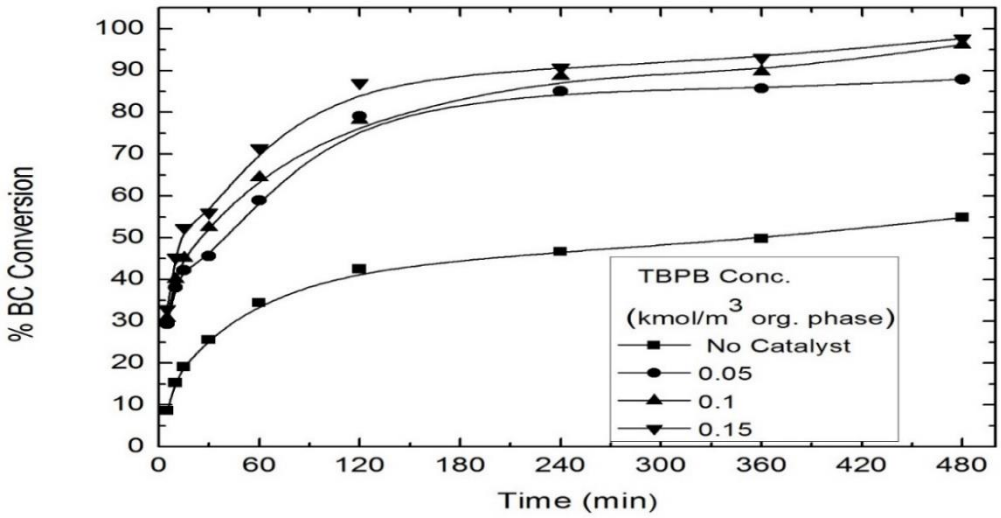
4.4.2 Effect of Catalyst Loading

Reaction was performed both in presence and absence of catalyst. A sudden increase in BC conversion from 45% in absence of catalyst to above 88% in presence of catalyst after 480 min of reaction was noticed. Then the catalyst concentration range was varied from 0.05 to 0.15 kmol/m^3 of organic phase and enhancement of BC conversion with catalyst loading was observed (Fig. 4.8 (a)). The enhancement factor of initial reaction rate at 5% conversion with increasing catalyst loading is shown in Table 4.1 below.

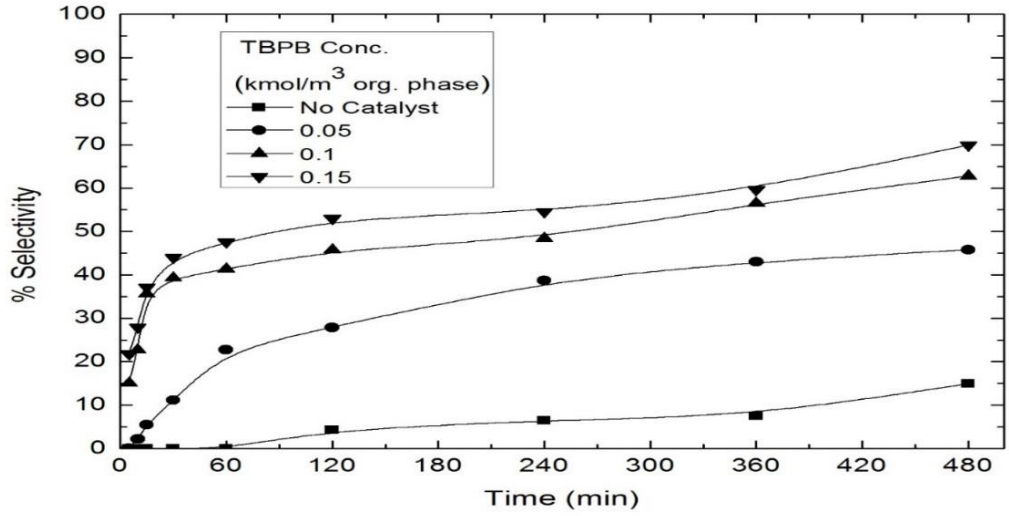
Table 4.1: Effect of Catalyst Loading on Initial Reaction Rate at 5% Conversion

Concentration of TBPB (kmol/m^3 org phase)	**Initial reaction rate (kmol/m^3s) at 5% Conversion**	**Enhancement factor**
0.00	0.001	-
0.05	0.012	12.63
0.10	0.014	14.75
0.15	0.015	15.80

Drastic increase of DBS selectivity from 15% in absence of catalyst to above 45% in catalyst presence was notice (Fig. 4.8 (b)). The same result was also obtained during modeling of catalyst intermediate. So it is concluded that at high catalyst concentration, sulfide catalyst active intermediate (QSQ) is a dominating specie responsible for DBS synthesis (reaction 13 and 15 of Scheme 4.2) rather than hydrosulfide catalyst intermediate (QSH) giving high DBS selectivity.



(a)



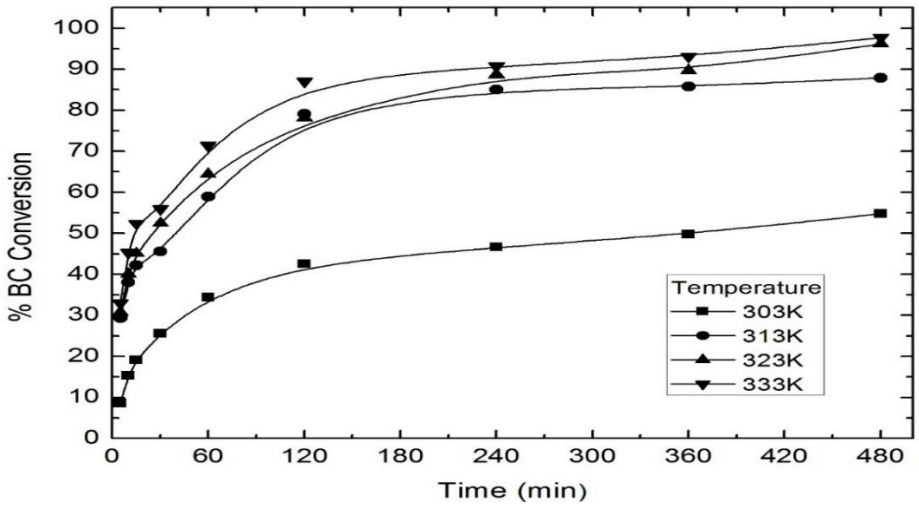
(b)

Figure 4.8: Influence of Catalyst Loading on (a) BC Conversion (b) DBS Selectivity Aqueous and Organic Phase Volume = 50 × $10^{-5}$$m^3$each, Sulfide Conc. = 1.5 kmol/m^3Aqu. Phase, BC moles = 0.261 mol, Temperature = 323K, Agitation speed = 1500 rpm, MDEA Conc. = 3.05 kmol/m^3

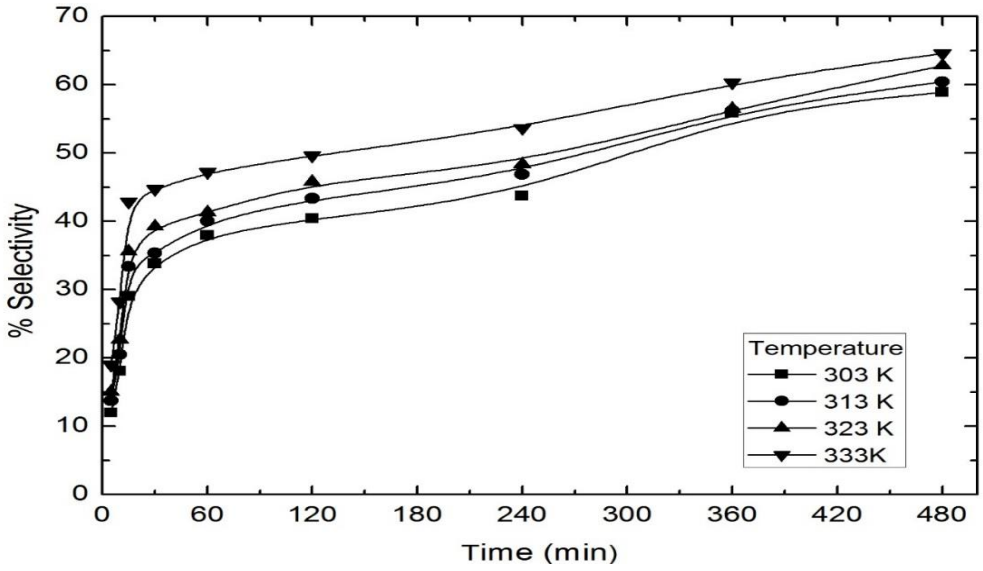
4.4.3 Effect of Temperature

The temperature range from 30-60^{0}C was selected to estimate consequence of temperature change on conversion and selectivity of product keeping other reaction conditions constant. The

expected nature of BC conversion increment with continuous increasing temperature was observed. Fig 4.9 (a) and (b) shows increase in BC conversion without significant increase in DBS selectivity.



(a)



(b)

Figure 4.9: Influence of Temperature on (a) BC conversion (b) DBS Selectivity Aqueous and Organic Phase Volume = 50 × 10^{-5} m^3 each, Sulfide Conc. = 1.5 kmol/m^3Aqu. Phase, BC moles = 0.261 mol, TBPB = 0.1 kmol/m^3 org phase, Agitation speed = 1500 rpm, MDEA Conc. = 3.05 kmol/m^3

Initial reaction rate at 5% BC conversion was calculated for Arrhenius plot of In (Initial Reaction Rate) Vs T^{-1}at various temperature where r is coefficient of correlation and s is standard deviation (Fig. 4.10). The activation energy, calculated from slope of Arrhenius plot, is found to be 47.69 kJ/mol.

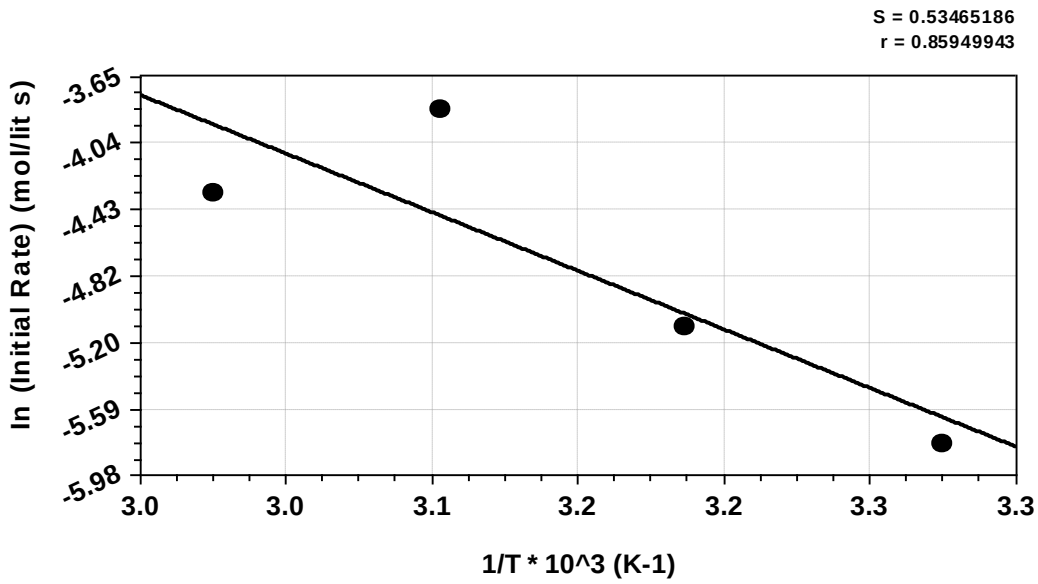
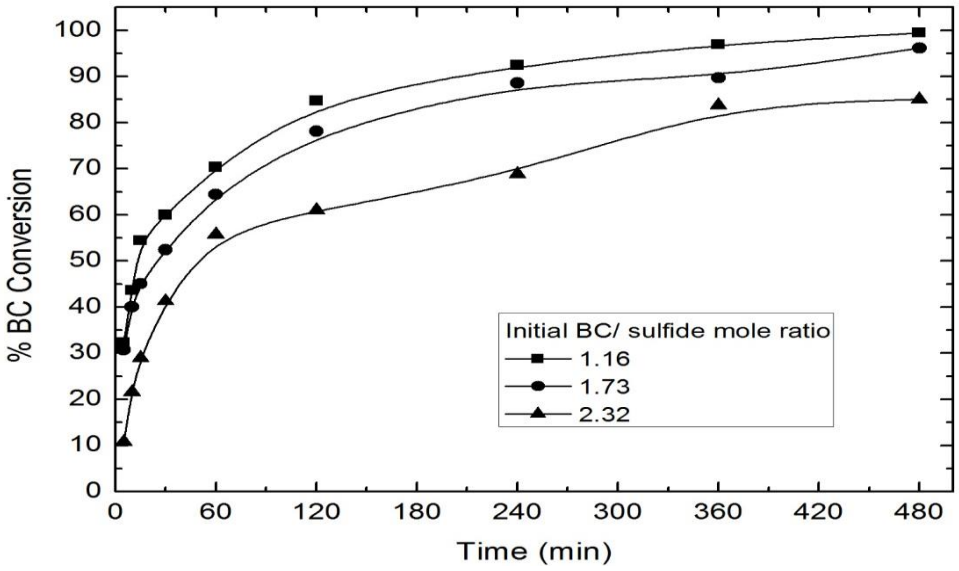


Figure 4.10: Arrhenius Plot of In (Initial Reaction Rate) vs 1/T

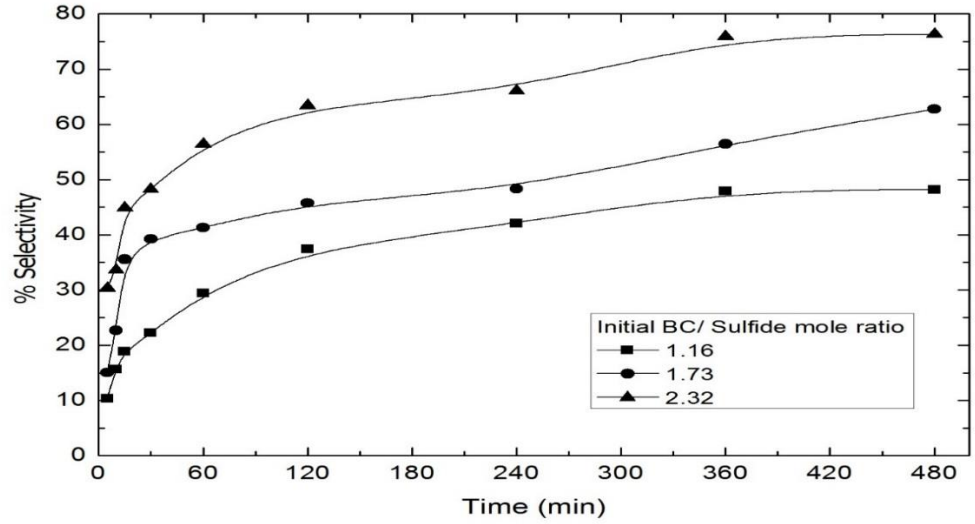
4.4.4 Effect of Organic Reactant BC

The concentration of BC was changed from 1.16-2.32 mole / sulfide mole as shown in Fig. 4.11 (a) keeping constant sulfide concentration. Decrease in BC conversion was noticed with gradual increase in BC/sulfide mole ratio due to unavailability of sufficient aqueous S^{2-} and HS^{-} anions in aqueous phase. So sulfide ions are considered as a limiting reactant.

In contrast to conversion, a sudden increase in DBS selectivity was observed at high BC/sulfide mole ratio (Fig. 4.11 (b)). 100% selectivity was noticed with 2.32 mole ratio at 480 min of reaction time. Increased selectivity was noticed due to conversion of BM to DBS in presence of excess BC via reaction 11 and 14 in Scheme 4.1. So condition is suitable for getting high DBS conversion. In present work, to get appreciable conversion as well as selectivity, 1.73 mole ratio is considered as optimum condition for further study.



(a)



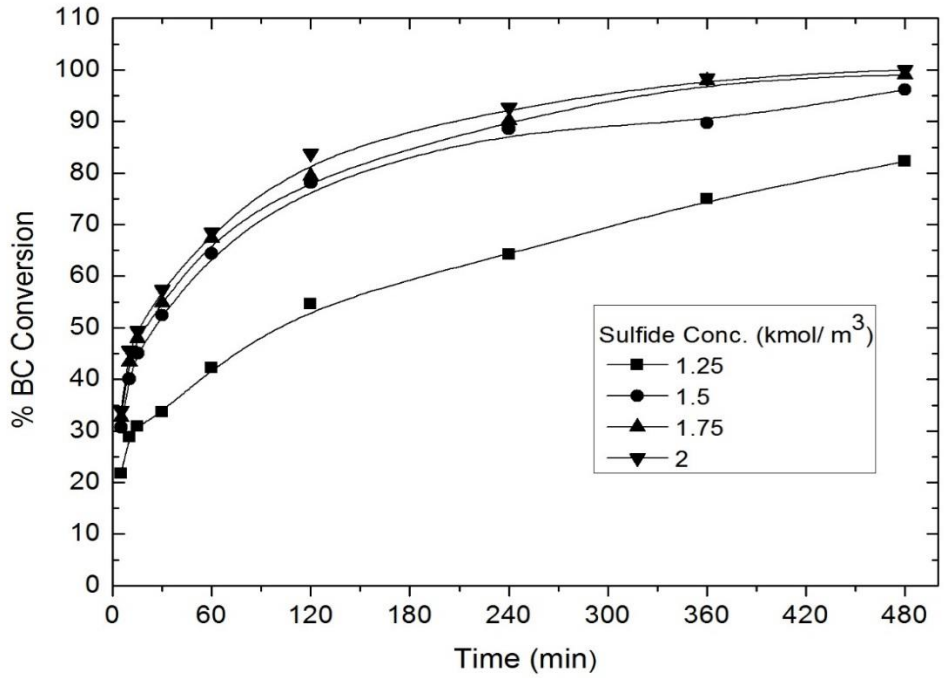
(b)

Figure 4.11: Influence of BC Concentration on (a) BC Conversion (b) DBS Selectivity Aqueous and Organic Phase Volume = 50 × 10^{-5} m^3 each, Sulfide Conc. = 1.5 kmol/m^3Aqu. Phase, TBPB = 0.1 kmol/m^3 org phase, Agitation speed= 1500 rpm, Temperature = 323K, MDEA Conc. = 3.05 kmol/m^3

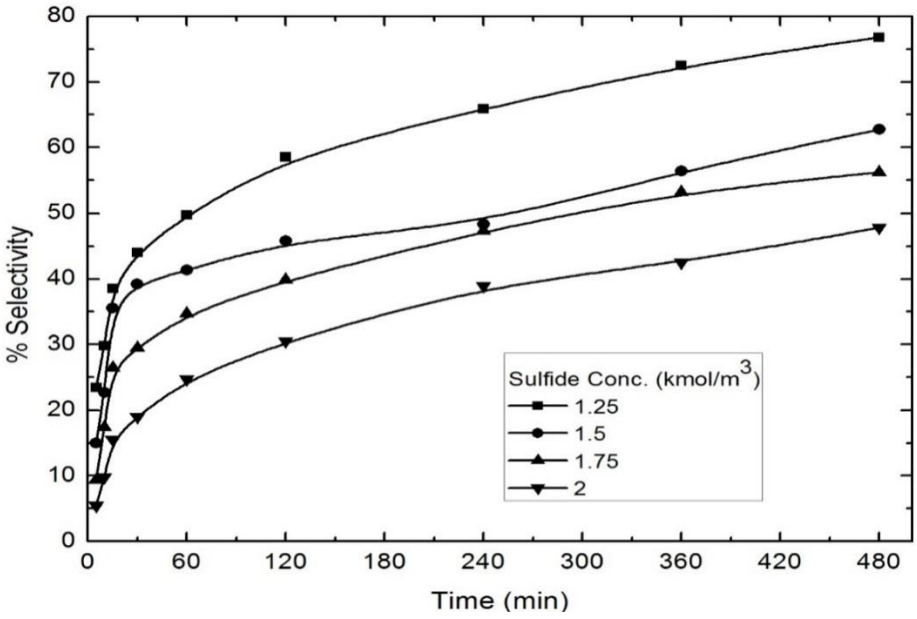
4.4.5 Effect of Sulfide Concentration

To determine the influence of sulfide concentration at fixed MDEA concentration in aqueous phase, MDEA/sulfide mole ratio was varied from 1.25 to 2 kmol/m^3. The increase in conversion from 82% to 100% was noticed in this variation range after 480 min of reaction due to increase in HS^- ions concentration in aqueous phase (Fig. 4.12 (a)).So here BC is considered as a limiting reactant. The opposite trend was observed for selectivity of DBS with increasing sulfide concentration shown in Fig 4.12 (b) below. Decrease in selectivity from 76 to 47% was recorded after 480 min of reaction time.

The decrease in selectivity was noticed because from the modeling, it is clear that high sulfide concentration is responsible for high HS^- ion concentration which in turn produces QSH catalyst active intermediates responsible for BM synthesis via reaction 12 of Scheme 4.2.



(a)



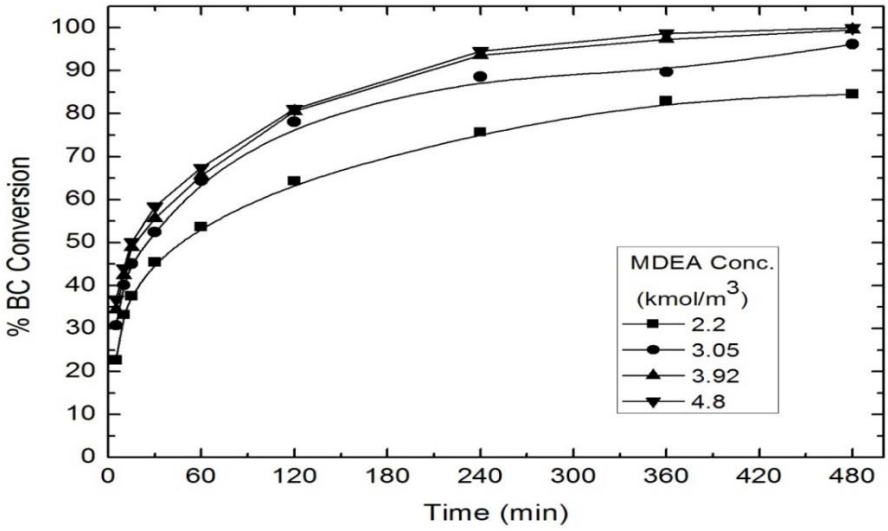
(b)

Figure 4.12: Influence of Sulfide Concentration on (a) BC Conversion (b) DBS Selectivity Aqueous and Organic Phase Volume = 50 × 10^{-5} m^3 each, BC moles = 0.261 mol, TBPB = 0.1 kmol/m^3 org phase, Temperature = 323K, Agitation speed= 1500 rpm, MDEA Conc. = 3.05 kmol/m^3

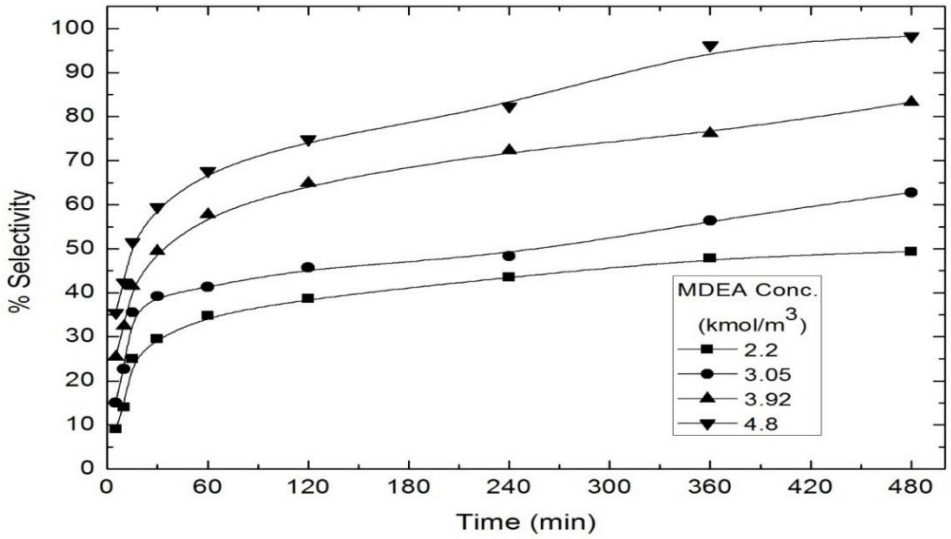
4.4.6 Effect of MDEA Concentration

The MDEA concentration was varied by taking 30 ml of known aqueous MDEA and sulfide solution (1.5 kmol/m^3 sulfide and 35 wt% MDEA) and then adding different concentration of aqueous MDEA solution to make 50 ml volume. The increase in not only conversion but selectivity was observed with increasing MDEA concentration in aqueous phase (Fig. 4.13 (a, b)).

In present work, MDEA act as an absorbent for H_2S absorption and does not interfere the synthesis reaction. But during the ionic equilibria of H_2O, MDEA and H_2S in aqueous phase, its concentration plays an important role. The concentration of sulfide anion (S^{2-}) increases compare to hydrosulfide anion (HS^-) with increasing MDEA concentration. From Scheme 4.2 and modeling, it is clear that S^{2-} anions are responsible for formation of QSQ catalyst intermediates which further reacts with 2 moles of BC to give DBS. So high concentration of sulfide anions (S^{2-}) not only increases conversion of BC but also increases DBS selectivity.



(a)



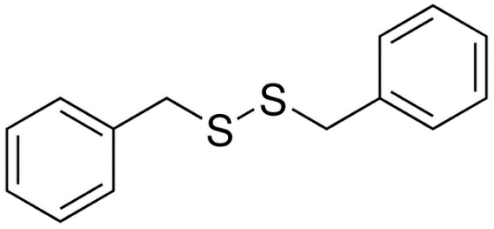
(b)

Figure 4.13: Influence of MDEA Concentration on (a) BC Conversion (b) DBS Selectivity Aqueous and Organic Phase Volume = 50 × 10^{-5}m^{3}each, Sulfide Conc. = 1.5 kmol/m^{3}Aqu. Phase, BC moles = 0.261 mol, TBPB = 0.1 kmol/m^3 org phase, Temperature = 323K, Agitation Speed= 1500 rpm, MDEA Conc. = 3.05 kmol/m^3

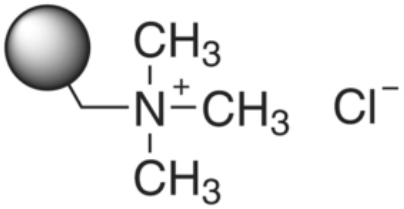
So from parametric study, it can be concluded that synthesis reaction is kinetically controlled reaction with negligible mass transfer resistance. The increased DBS selectivity can be obtained at high concentrations of catalyst, BC and MDEA. The opposite is true for high selectivity of BM at high sulfide concentration in aqueous phase.

CHAPTER 5

SYNTHESIS OF DIBENZYL DISULFIDE UNDER LIQUID-LIQUID-SOLID PTC



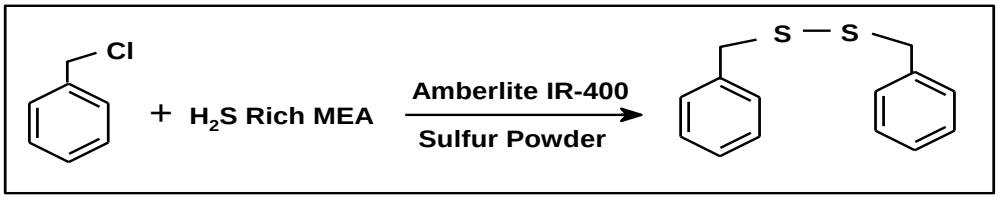
DBDS



Amberlite IR-400

5.1 INTRODUCTION

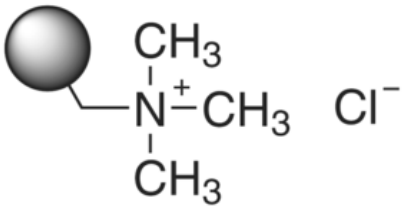
Dibenzyl Disulfide was synthesized from reaction between benzyl chloride in organic solvent toluene and H_2S rich ethanolamine (MEA) as an aqueous phase using Amberlite IR-400 as a solid catalyst and sulfur powder in aqueous phase under Liquid-Liquid-Solid (L-L-S) PTC at 50^0C. Disulfide and other polysulfide can easily be obtained by adding sulfur powder in sulfide rich aqueous solution (Sonavane et al., 2007). Here the selective synthesis of DBDS by reducing unwanted side products like BM, DBS and polysulfide was obtained by adding adequate quantity of sulfur powder in aqueous phase in batch reactor shown in Fig 3.2. Scheme 5.1 represents the overall synthesis reaction of DBDS synthesis.



Scheme 5.1

In current work, effect of agitation speed and temperature was studied to find out mass transfer resistance and activation energy respectively. Other reaction parameters like effect of MEA and BC concentration, catalyst loading, sulfide concentration and sulfur powder loading in aqueous phase were also studied to established exact mechanism of DBDS synthesis reaction.

DBDS is a white crystalline powder used in manufacturing fragrance compounds, high pressure lubricants additive and corrosion inhibitors. Disulfides are more stable for organic reactions like alkylation, oxidation, acylation as compare to thiols therefore thiol group is now a day commercially protected in disulfide forms. Also disulfide can easily be converted to thiols. For this reason, many techniques are developing for selective synthesis of disulfides (Thurow et al., 2011; Bandgar et al., 2001). The structural formula of Amberlite IR-400, a quaternary ammonium ion exchange resin, is shown in Scheme 5.2.



Scheme 5.2

5.2 MECHANISM

The mechanism of reaction between BC with H_2S rich MEA and sulfur powder in aqueous phase using Amberlite IR-400 as a PT catalyst is shown in Scheme 5.3.Generally aqueous phase reactions are faster compare to organic phase reactions, so an ionic equilibrium exists in aqueous phase between RNH_2 (MEA) -H_2O-H_2S which results in formation of three active inorganic nucleophiles namely hydroxide $(OH)^-$, sulfide (S^{2-}) and disulfide (S_2^{2-}) as represented in aqueous phase. In present system, hydrosulfide anion (HS^-) is not expected to form due to presence of sulfur powder in aqueous phase. Sulfur shifts ionic equilibrium to right giving only sulfide (S^{2-}) and disulfide (S_2^{2-}) anions in aqueous phase. The product was obtained from both catalytic and non-catalytic contribution.

5.2.1 Non- catalytic Contribution

The non-catalytic mechanism is similar to mechanism explained in Chapter 4 during synthesis of BM and DBS. Ethanolamine sulfide ($(RNH_3)_2S$) and ethanolamine disulfide ($(RNH_3)_2S_2$), formed in aqueous phase via reaction 2-3 in Scheme 5.3, are insoluble in organic phase. So they are expected to react with BC in aqueous-organic interface to give DBS and DBDS respectively as shown in reaction 7-9. Due to 2nd order reaction rate of nucleophilic reaction, DBS is expected to form via formation of intermediate product $C_6H_5CH_2SNH_3R$ which again reacts with BC to give desired DBS. The formed product travels from interface to organic phase from where selective separation of products takes place.

5.2.2 Catalytic Contribution

Mass transfer and surface reaction are two important steps in presence of solid catalyst in L-L-S PTC (Satrio et al., 2000). Synthesis steps involve:

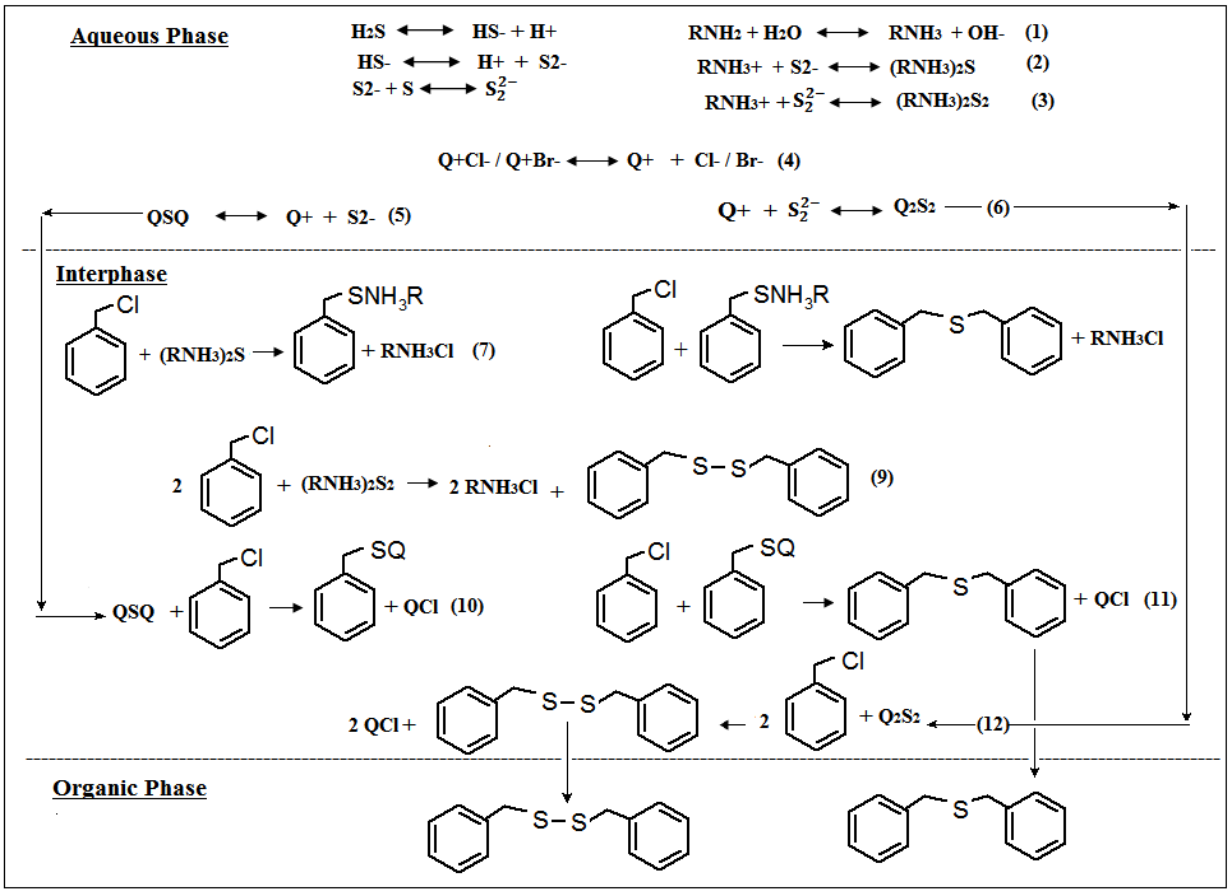
Step 1: Diffusion of aqueous anions $S^{2-}$and S_2^{2-} from bulk of aqueous phase to PT catalyst.

Step 2: Ion exchange reaction of these nucleophiles with catalyst cation (Q^+) to form catalyst active intermediate QSQ and Q_2S_2 as shown in reaction 4-6 and leaving Cl^- anion.

Step 3: Diffusion of organic reactant BC from bulk of organic phase to TP catalyst.

Step 4: Synthesis reaction of BC at catalyst active site present at aqueous organic interphase to give desired products (reaction 10-12).

Step 5: Diffusion of anion Cl^- and product from interface to aqueous and organic phase respectively as shown in scheme below.



Scheme 5.3: Reaction Mechanism

5.3 PARAMETRIC STUDY

5.3.1 Influence of Stirring Speed

The speed of agitation was varied from 1000 to 2000 rpm to determine effect of mass transfer resistance of reactants. Fig. 5.1 shows that conversion is practically same in all stirring speed. Therefore, beyond 1500 rpm, increase in stirring speed has no influence on conversion, so

reaction can be safely considered as a kinetically controlled reaction. Thus, the further synthesis was carried out at 1500 rpm to remove mass transfer resistance.

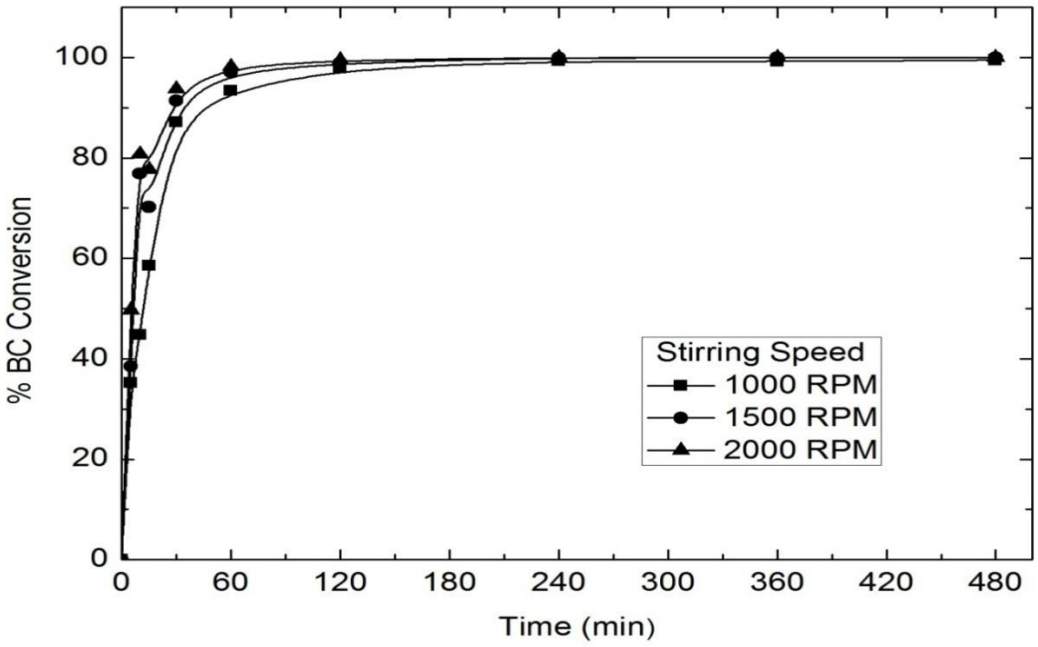


Figure 5.1: Influence of Agitation Speed on BC Conversion Volume of aqueous and organic phase = 50× 10^{-5}m^{3}each; BC mole = 0.261 mol; Catalyst conc. = 0.29 kmol/m^3 org phase;Sulfide Conc. = 2.53kmol/m^3; MEA/H_2S mole ratio = 2.28; Temperature = 323 K; Sulfur loading= 3gm.

5.3.2 Influence of Sulfur Loading

Disulfide and polysulfide anions can easily be obtained by dissolving elemental sulfur powder in S^{2-} anion rich aqueous phase (Sonavane et al., 2007).The effect of this elemental sulfur loading on synthesis of DBDS was investigated by adding different concentration of sulfur powder in H_2S rich MEA. The color of aqueous MEA changed from greenish to reddish brown indicating formation of polysulfide anions S_x^{2-} (where x = 1, 2, 3, 4) depending on sulfur loading.

At low sulfur loading, hydrosulfide (HS^-) and sulfide (S^{2-}) ions are the dominating sulfur species giving BM and DBS respectively as a product (Sen et al., 2007). So selectivity at 1 and 2 gm of sulfur loading was found to be low and it was almost negligible in absence of sulfur loading (Fig. 5.2). Whereas at high sulfur loading, polysulfide anions $S_{3,4,5}^{2-}$ are the dominating sulfur species giving unwanted product trisulfidse and polysulfides (Sonavane et al., 2007), giving again low DBDS selectivity. 100% selectivity of DBDS was observed at 3 gm of sulfur due to presence

of only disulfide anions S_2^{2-}. So 3 gm of sulfur was considered as an optimum reaction parameter and further experiments were performed at this condition.

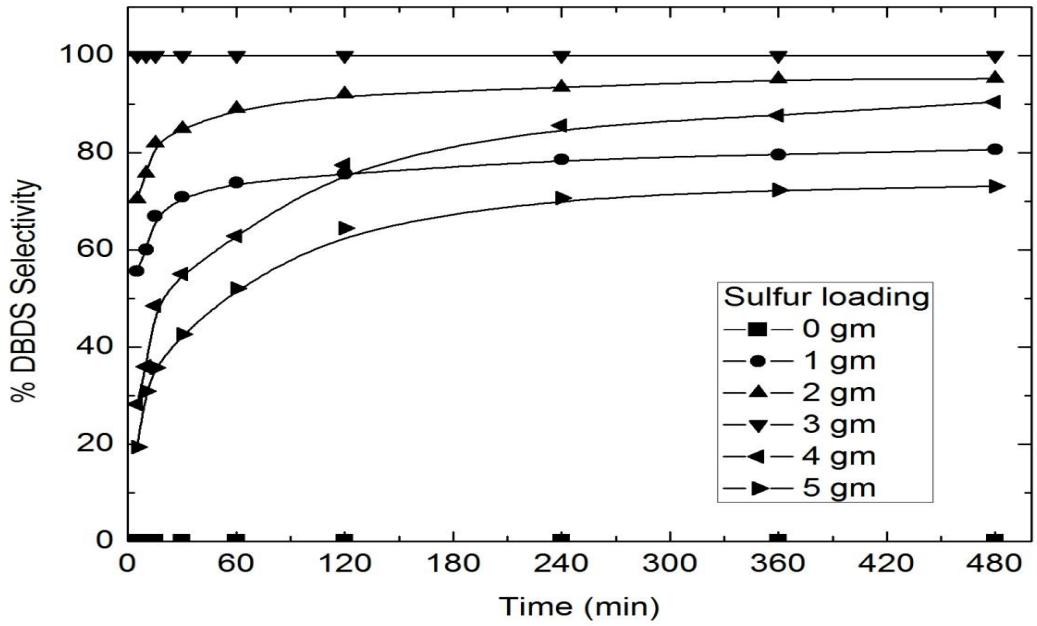


Figure 5.2: Effect of Sulfur Powder Loading on DBDS Selectivity Volume of aqueous and organic phase = 50× 10^{-5}m^{3}each; BC mole = 0.261 mol; Catalyst conc. = 0.29 kmol/m^3 org phase; Sulfide Conc. = 2.53 kmol/m^3; MEA/H_2S mole ratio = 2.28; Temperature = 323 K; Agitation Speed= 1500 rpm

5.3.3 Influence of Catalyst Concentration

The influence of catalyst loading on BC conversion was determined both in presence and absence of catalyst keeping other reaction condition constant (Fig. 5.3). It was noticed that BC conversion was only 58% in absence of catalyst even after 480 min of reaction. A drastic increase in BC conversion was observed with catalyst loading and conversion was observed to increase with increase in catalyst loading.

In the presence of catalyst, Sulfide (S^{2-}) and disulfide anions of aqueous phase react with active site of catalyst (quaternary ammonium halide, Q^+) inside the catalyst to give catalyst active intermediates QSQ and Q_2S_2 respectively. When organic phase diffuses inside the catalyst, these catalyst intermediates then react with BC to give DBS and DBDS respectively (Satrio et al., 2000). With increase in catalyst concentration, more catalyst intermediates are formed, giving increased conversion of BC according to reaction 10 to 12 in Scheme 5.3. In present work, 100% selectivity

of DBDS was observed due to adequate quantity of sulfur powder in aqueous phase giving only disulfide S_2^{2-} anions.

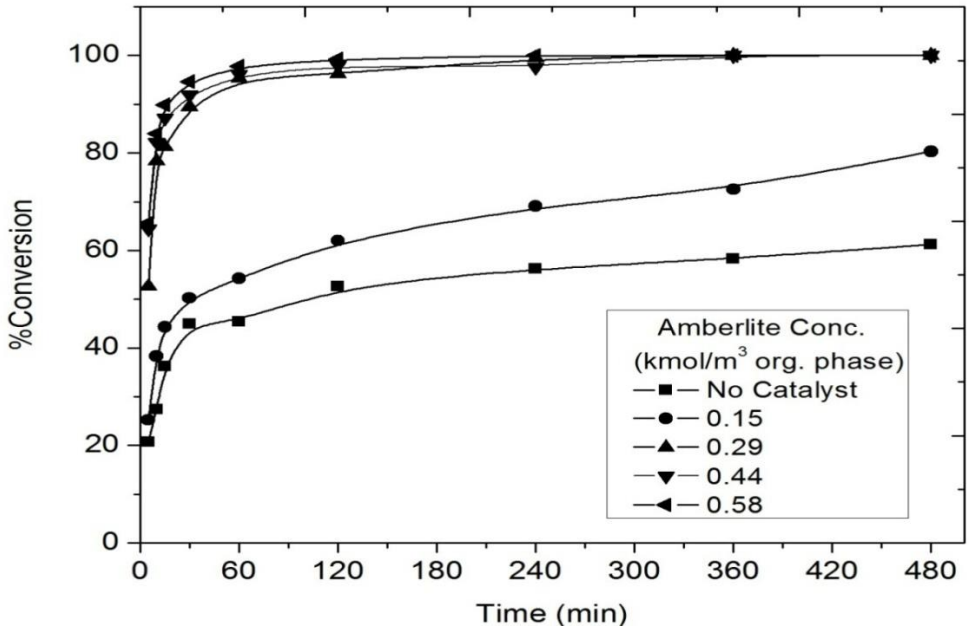


Figure 5.3: Influence of Catalyst Loading on BC Conversion Volume of aqueous and organic phase = 50 × 10^{-5}m^{3}each; BC mole = 0.261 mol; Sulfide Conc. = 2.53 kmol/m^3; MEA/H_2S mole ratio = 2.28; Temperature = 323 K; Sulfur loading= 3gm, Agitation Speed= 1500 rpm

Table 5.1 shows enhancement of initial reaction rate compared to absence of Amberlite catalyst. Enhancement factor indicates the importance of Amberlite IR-400 as a PT catalyst in DBDS synthesis.

Table 5.1: Effect of Catalyst Loading on Initial Reaction Rate at 5% Conversion

Concentration of Amberlite IR-400 (kmol/m^3 org phase)	Initial reaction rate (kmol/m^{3}s) at 5% Conversion	Enhancement factor
0	0.00479	-
0.15	0.00498	1.2
0.29	0.00887	1.9
0.44	0.0138	2.9
0.58	0.0147	3.1

In order to calculate order of reaction with respect to Amberlite IR-400 catalyst, natural logarithm of initial reaction rate of different catalyst concentration was plotted against natural logarithm of Amberlite concentration (Fig. 5.4). The order of reaction, obtained from slope of plot where r is coefficient of correlation, was 0.83 which is considered as 1st order with respect to catalyst concentration.

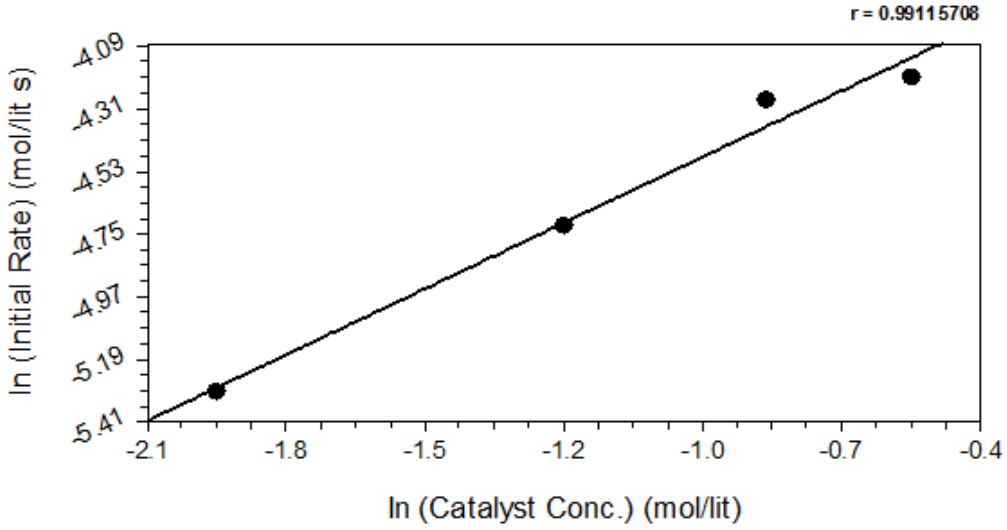


Figure 5.4: In (Initial Reaction Rate) Vs In (Catalyst Concentration)

5.3.4 Influence of Temperature

To determine the influence of temperature on BC conversion, temperature was varied from 303 to 333K keeping other experimental condition constant. The expected nature of increased BC conversion with increase in temperature was noticed according to transition theory (Fig. 5.5).

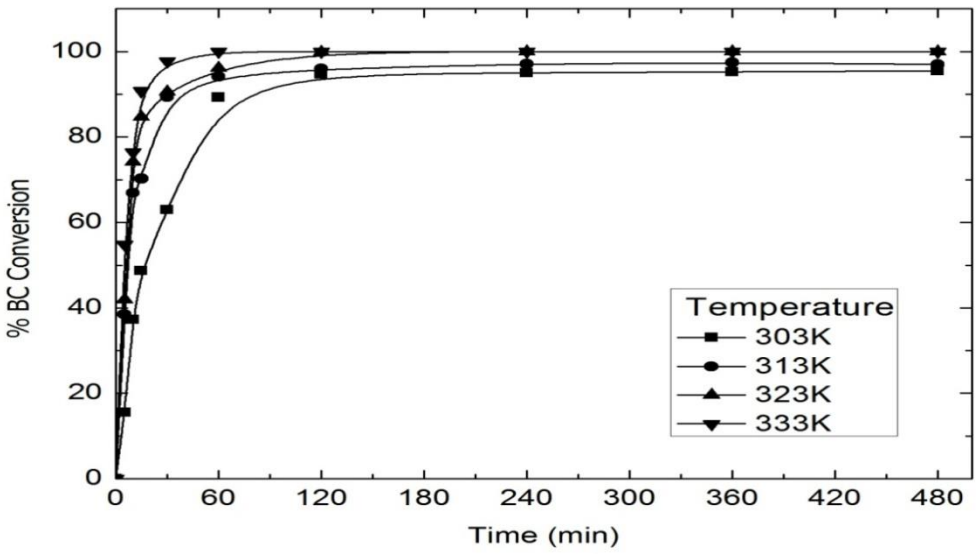


Figure 5.5: Influence of Temperature on BC Conversion Volume of aqueous and organic phase = 50× $10^{-5}$$m^3$each; BC mole = 0.261 mol; Catalyst conc. = 0.29 kmol/m^3 org phase; Sulfide Conc. = 2.53 kmol/m^3; MEA/H_2S mole ratio = 2.28; Sulfur loading= 3gm, Agitation Speed= 1500 rpm

Different temperature initial reaction rate was calculated for Arrhenius plot. Natural logarithm of initial reaction rate was plotted against 1/T (K^{-1}) and activation energy was calculated slope of the Fig. 5.6 where r is coefficient if correlation and s is standard deviation. The apparent activation energy of kinetically controlled reaction was obtained as 22.4 kJ/mol.

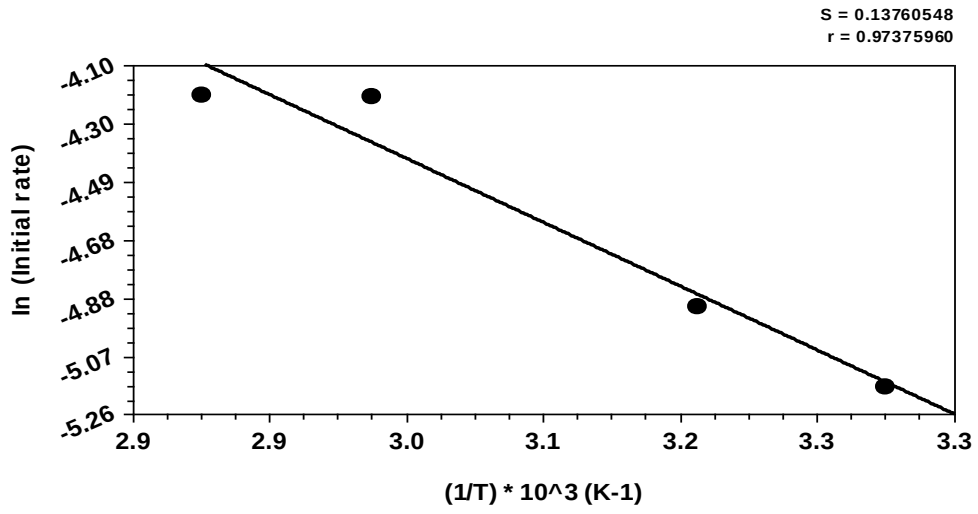


Figure 5.6: Arrhenius plot of In (Initial Reaction Rate) vs 1/T

5.3.5 Influence of Benzyl Chloride Concentration

The effect of reactant concentration was investigated by varying organic reactant concentration (BC) keeping constant sulfide concentration in aqueous phase i.e. different initial BC/ Sulfide mole ratio. Decrease in BC conversion was noticed with increase in ratio due to limitation of sulfide anions present in aqueous phase (Fig. 5.7). At low BC/sulfide mole ratio (0.7 to 1.04), 100% conversion was obtained but reduced to 94% for 1.39. So it is concluded that low initial BC/ sulfide mole ratio is preferable for present work to get 100% conversion.

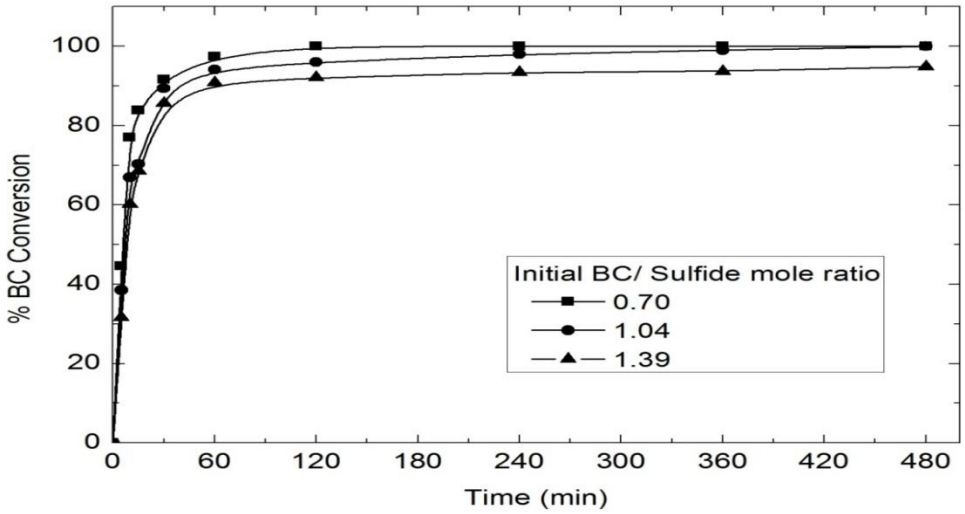


Figure 5.7: Influence of BC Concentration on Conversion Volume of aqueous and organic phase = 50× $10^{-5}$$m^3$each; Catalyst conc. = 0.29 kmol/m^3 org phase; Sulfide Conc. = 2.53 kmol/m^3; MEA/H_2S mole ratio = 2.28; Temperature = 323 K; Sulfur loading= 3gm, Agitation Speed= 1500 rpm

5.3.6 Influence of Sulfide Concentration

Sulfide concentration of aqueous phase was changed from 1.75 to 2.5 kmol/m^3 keeping constant MEA concentration (35 wt %). There is slight decrease in conversion was notice with decreasing sulfide concentration but almost 100% conversion was obtained in all sulfide range at 480 min of reaction time (Fig. 5.8). Negligible influence on conversion was noticed with increasing sulfide concentration, therefore sulfide concentration is not considered as a manipulating parameter of BC conversion in present study.

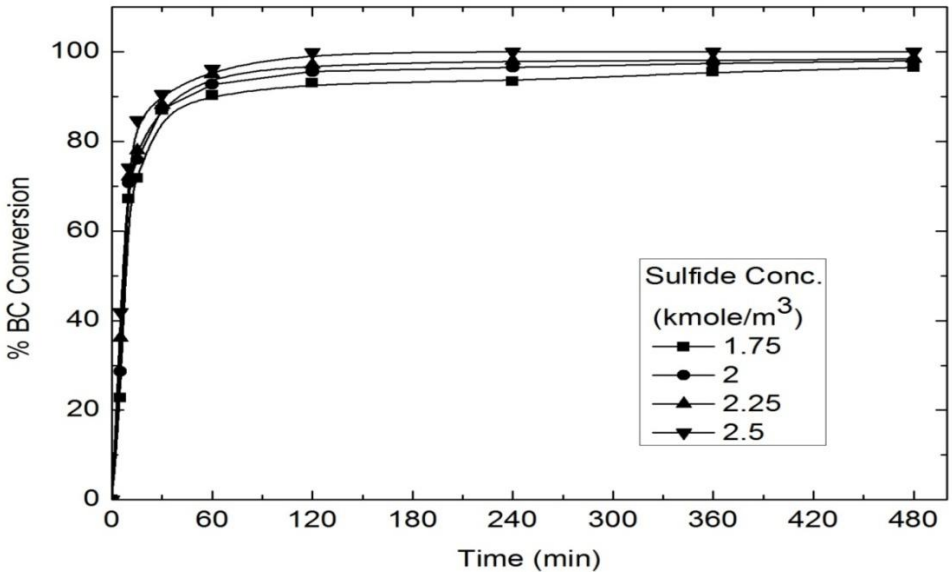


Figure 5.8: Influence of Sulfide Concentration on BC Conversion Volume of aqueous and organic phase = 50× $10^{-5}$$m^3$each; BC mole = 0.261 mol; Catalyst conc. = 0.29 kmol/m^3 org phase; MEA/H_2S mole ratio = 2.28; Temperature = 323 K; Sulfur loading= 3gm, Agitation Speed= 1500 rpm

5.4 CATALYST RECOVERY AND REUSE

After completion of synthesis process, agitation was stopped and aqueous and organic phases were allowed to settle down. Organic phase, present on top of aqueous phase, containing product was removed and Amberlite catalyst was allowed to settle down in aqueous phase. The catalyst present in aqueous phase was first recovered using filter paper. Then it was first washed with acetone to remove organic traces, then with water and 50% aqueous sodium chloride (NaCl) solution. After washing, catalyst was dried at 50^0C in oven to remove any adsorbed substance present on it. For each run, makeup catalyst was added with recovered catalyst and was reused in kinetic run four times and data were obtained shown in Fig. 5.9.

From the figure, it is seen that reusability of Amberlite is excellent up to four uses. But in every run, decrease in conversion was observed due to loss of catalyst in aqueous and organic phase and during catalyst washing process.

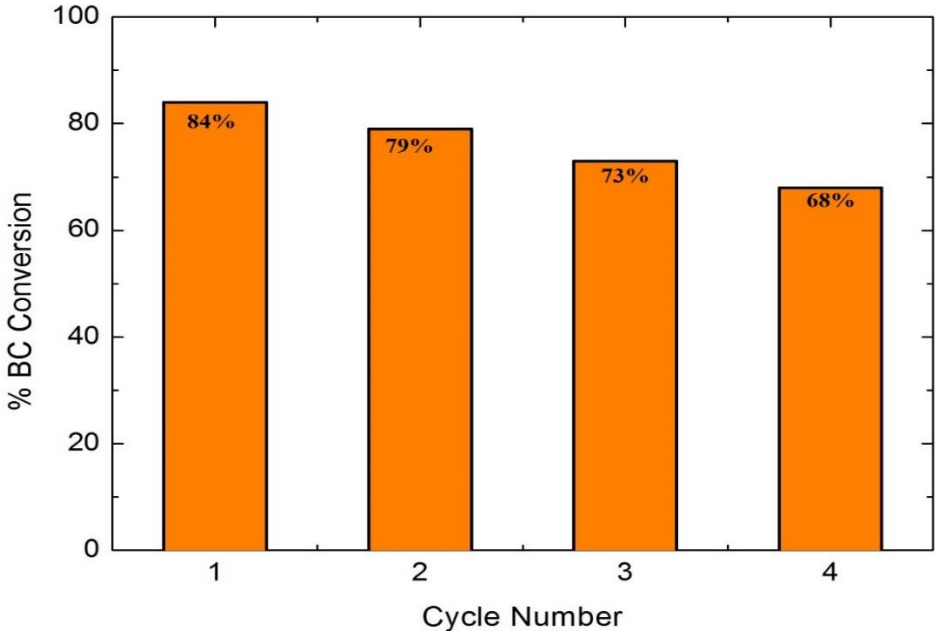


Figure 5.9: Recovery and Reuse of Catalyst Volume of aqueous and organic phase = 50× $10^{-5}$$m^3$each; BC mole = 0.261 mol; Catalyst conc. = 0.29 kmol/m^3 org phase; MEA/H_2S mole ratio = 2.28; Temperature = 323 K; Sulfur loading= 3gm, Agitation Speed= 1500 rpm

CHAPTER 6

CONCLUSION

CONCLUSION

In the present work, H_2S rich alkanolamine was used for synthesis of fine chemicals for enhancing utilization of H_2S present in various gas streams. H_2S was prepared in Kipp's apparatus in laboratory and then absorbed in alkaline solution. Ammonia was not selected as an absorbent due to its high partial pressure and difficulty in regeneration. So H_2S was absorbed in 30-35% aqueous alkanolamine (MEA/MDEA). Then reaction was performed in baffled mechanically agitated glass batch reactor. Sulfide concentration of H_2S rich aqueous alkanolamine was measured using Iodometric titration method. The concentration of organic sample was measured using GC-MS.

In first synthesis, DBS and BM were synthesized from H_2S rich aqueous MDEA solution and BC in organic phase using TBPB as a PT catalyst under L-LPTC mode. The concentration of ions and catalyst active intermediates in aqueous and organic phase was measured by solving simultaneous equations in MATLAB SOFTWARE. From the modeling, it was noticed that sulfide is dominating sulfur specie at high MDEA concentration responsible for QSQ catalyst active intermediate which in turn give high selectivity of DBS. The opposite is true for high sulfide concentration giving BM synthesis via generation of QSH catalyst intermediate.

100% conversion was recorded in all range of stirring speed above 1000 rpm indicating absence of mass transfer resistances. Therefore, 1500 rpm was selected as optimum reaction parameter for further study. High concentration of MDEA, catalyst and BC was found to be suitable for high DBS selectivity. Decrease in BC conversion was noticed at its high concentration due to limitation of sulfide and hydrosulfide ions in aqueous phase. The activation energy of kinetically control reaction, calculated from Arrhenius plot, was found to be 47.69kJ/mol.

Then system was modified by adding adequate quantity of elemental sulfur powder in aqueous phase for synthesis of DBDS. It was synthesized from H_2S rich aqueous MEA solution with BC in organic phase using Amberlite IR-400 as a solid PT catalyst under L-L-S PTC mode. It was observed that sulfur loading shifts H_2S aqueous ionic equilibrium to the right giving polysulfides ions. 100% selectivity of DBDS was obtained at 3 gm of sulfur loading. Mass transfer resistance obtained in both the synthesis was negligible indicating kinetically controlled reactions. 100% conversion was noticed with high catalyst and low BC concentration. There was no significant effect of sulfide concentration on conversion. The activation energy obtained for DBDS

synthesis, from slope of Arrhenius plot, was 22.4kJ/mol. Synthesis of DBDS was found to be first order with respect to catalyst concentration.

Since Amberlite is a solid catalyst, it was recovered and reused. It was first recovered using filter paper. Then it was first washed with acetone to remove organic traces, then with water and 50% aqueous sodium chloride (NaCl) solution. After washing, catalyst was dried at 50^0C in oven to remove any adsorbed substance present on it. Recovered catalyst was reused 4 times in DBDS synthesis with successive decrease in conversion in each run due to loss of catalyst with aqueous and organic phase during washing.

CHAPTER 7

FUTURE SCOPE

In present work, value added chemicals like DBS and DBDS was synthesized using H_2S rich aqueous phase. First DBS was synthesized using BC in organic solvent toluene and H_2S rich MDEA solution using TBPB as PT catalyst in L-L mode. Then system was modified for DBDS synthesis by adding elemental sulfur powder in H_2S rich MEA solution using amberlite IR-400 as PT catalyst under L-L-S PTC. Parametric study was done on both the system for increasing conversion of BC and selectivity of product. But there are some more things should be tried but not performed due to lack of facilities and opportunity. Some of them are discussed below:

7.1 EFFECT OF SOME OTHER PARAMETERS

Since the formation of ions in aqueous phase depend upon pH of alkanolamine, effect of different pH on conversion of BC and selectivity of DBS need to be evaluated. Similarly, since the transfer of catalyst intermediate from aqueous to organic phase depends on saturation of aqueous phase, effect of different co-catalyst like NaCl and base like NaOH in aqueous phase need to be find out for better selectivity of product.

Synthesis of DBS and DBDS should also be carried out using some other organic solvents like dodecane, n-heptane etc. Selection of solvent is very important since it effect the mass transfer barrier between aqueous and organic phase and also responsible for some side reactions like hydrolysis.

7.2 USE OF L-L-L PTC FOR CATALYST RECOVERY

In present work, catalyst was not recovered during DBS synthesis due to difficulty of separation of product and catalyst from organic solvent. This problem can be solved by creating a catalyst rich layer in between aqueous and organic phase either by increasing catalyst concentration or by saturating aqueous phase. This catalyst rich layer can easily be separated and reused for further synthesis. So synthesis of DBS should also be performed using L-L-L PTC.

7.3 SYNTHESIS OF POLYSULFIDES

During DBDS synthesis, it was observed that selective synthesis of polysulfide can be possible by adding adequate sulfur powder in H_2S rich aqueous phase. So synthesis of trisulfides and polysulfides are also possible by this technique.

7.4 LARGE SCALE APPLICATION OF PRESENT STUDY

The present work need to be performed in large reactors before using it in industrial scale. An efficient and economical process like distillation, absorption need to ne find out for catalyst recovery and product separation from organic phase for DBS synthesis using L-L PTC.

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EDUCATION

- B.Tech. in Petro Chemical Engineering from **Dr. Babasaheb Ambedkar Technological University, Lonere**, in 2011 with **8.4 CGPA**
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DECLARATION

I hereby declare that the information furnished above is true to the best of my knowledge.